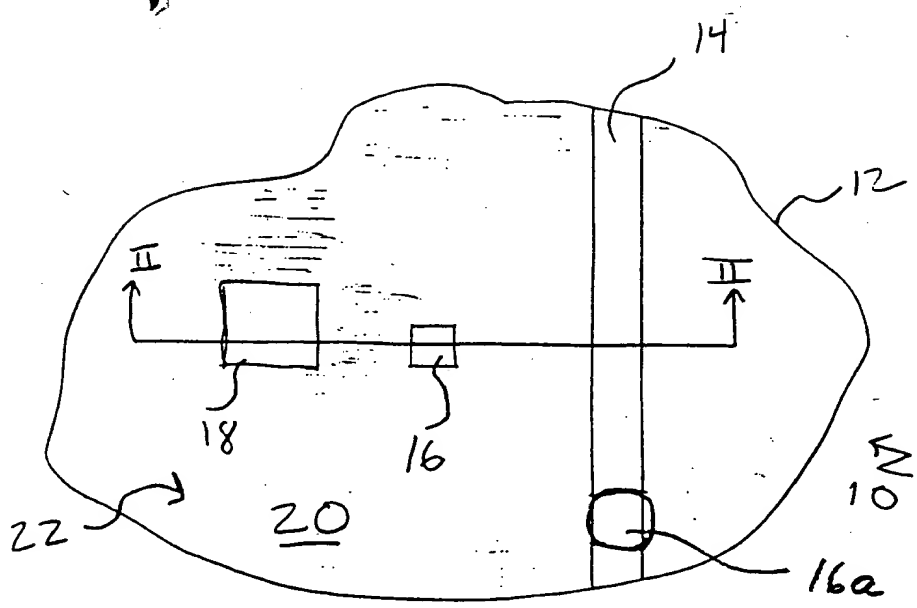

14
12
II
II
18
16
10
22
20
16a

FIG. 1

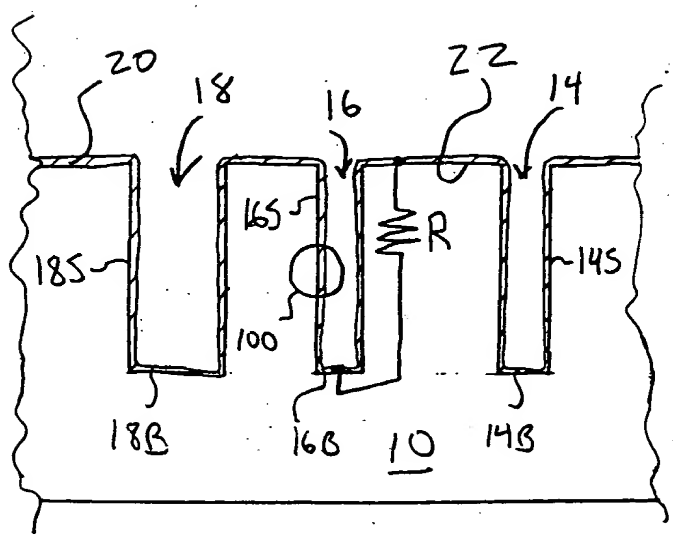

20
18
16
22
14
16S
R
18S
14S
100
18B
16B
10
14B

FIG. 2

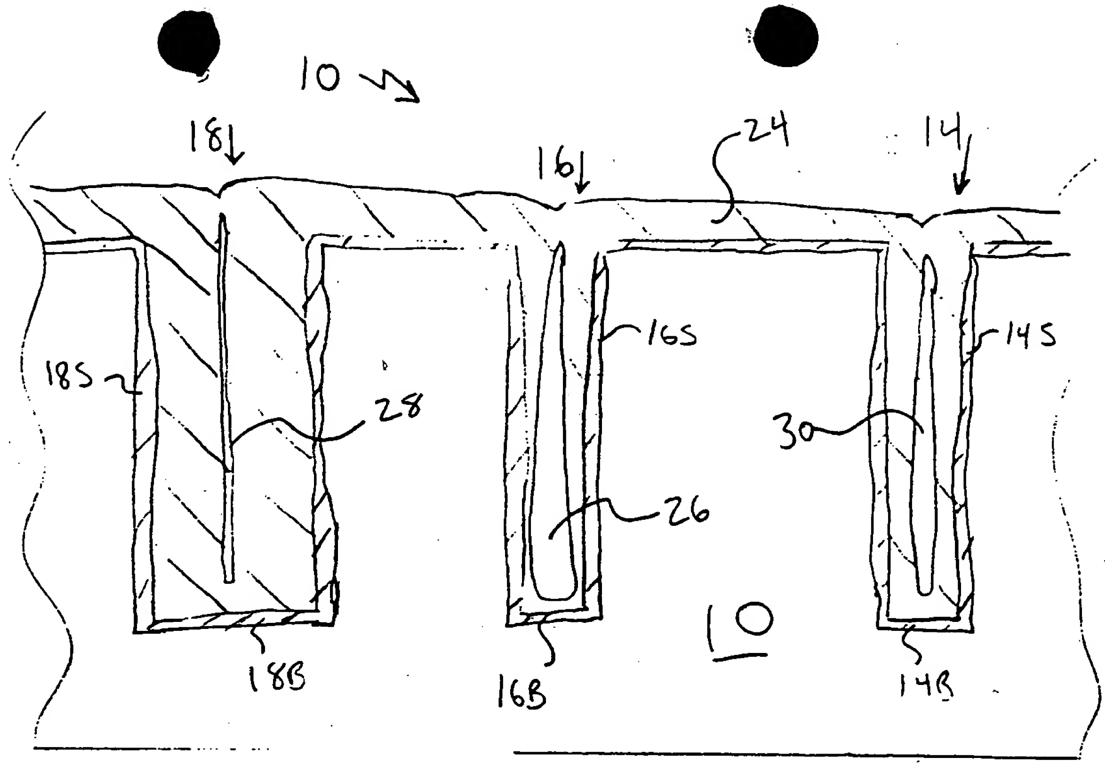

10
18
16
24
14
18S
16S
14S
28
30
26
18B
16B
14B
10

FIG. 4

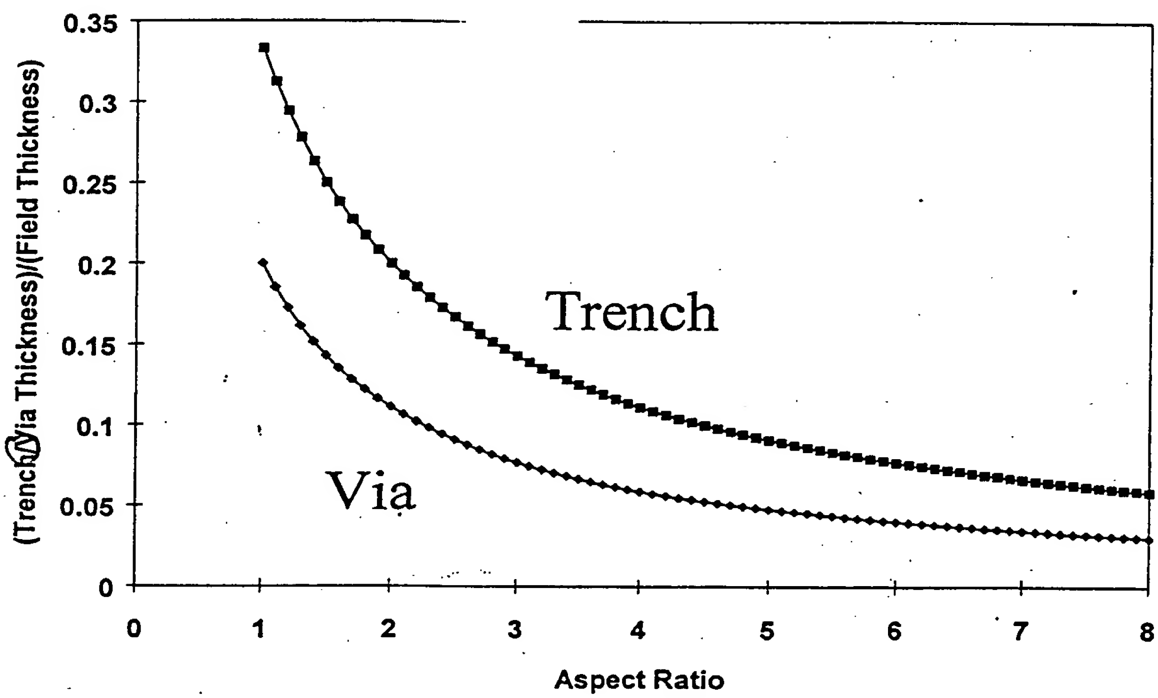

(Trench/Via Thickness)/(Field Thickness)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
7
8
Aspect Ratio
Trench
Via

FIG. 3

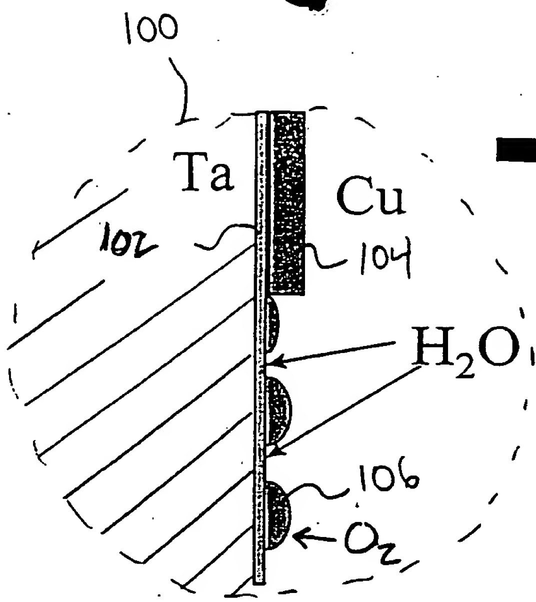


FIG. 5A

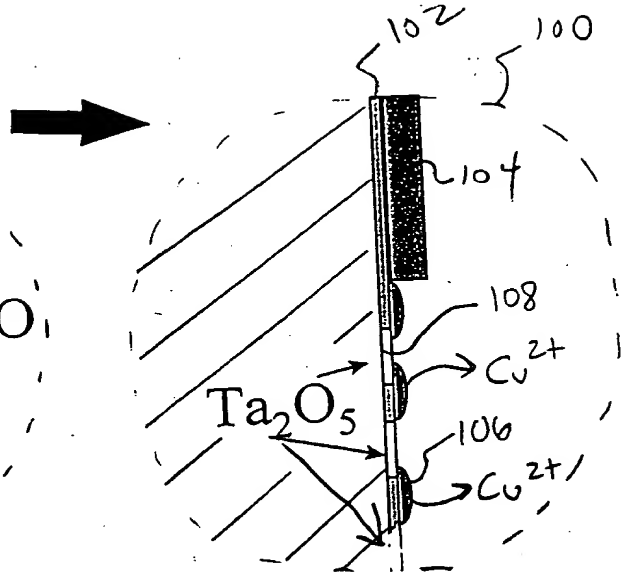


FIG. 5B

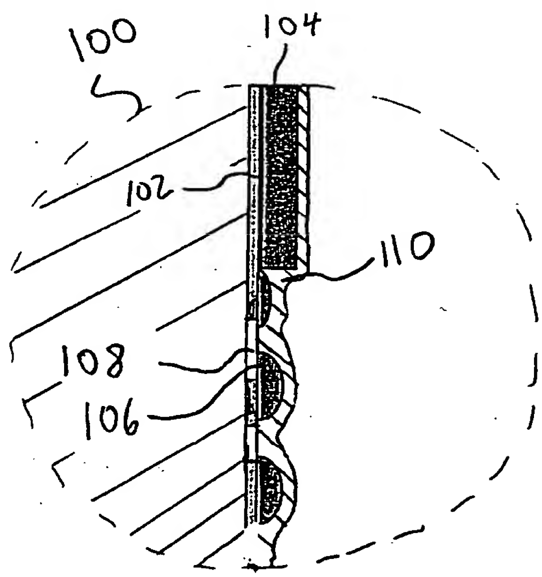


FIG. 6

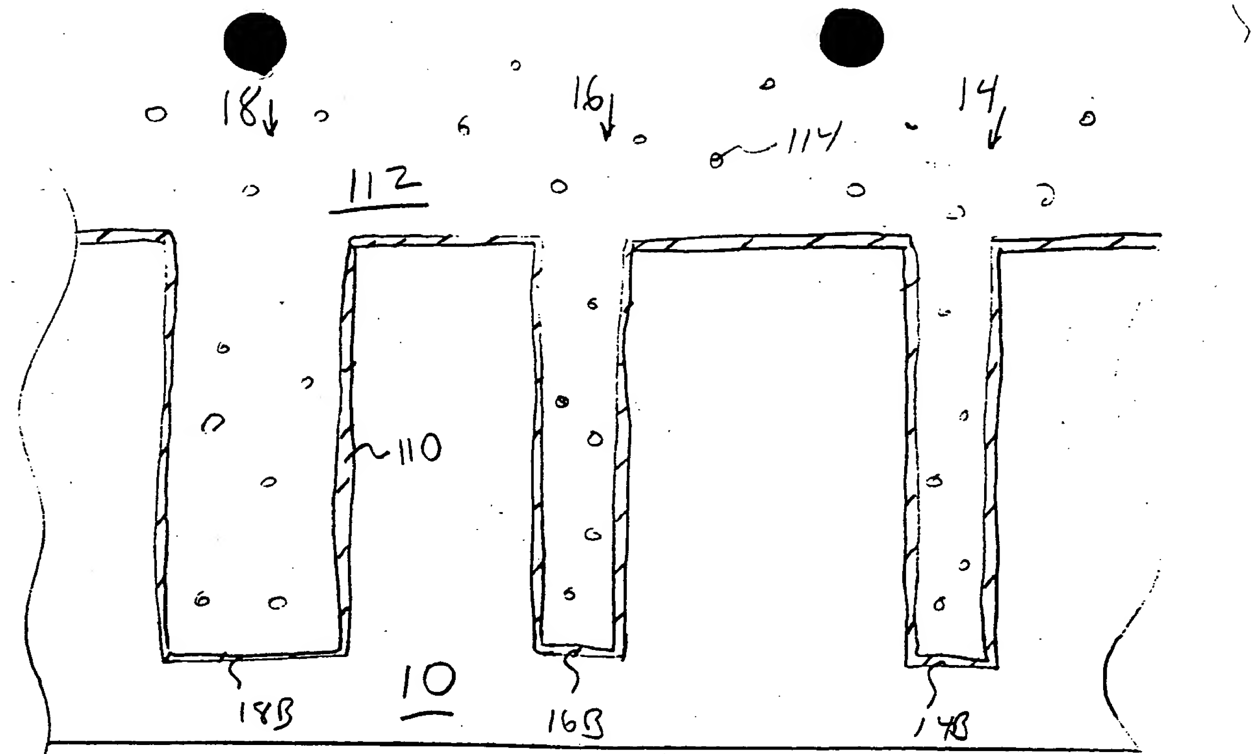


FIG. 7

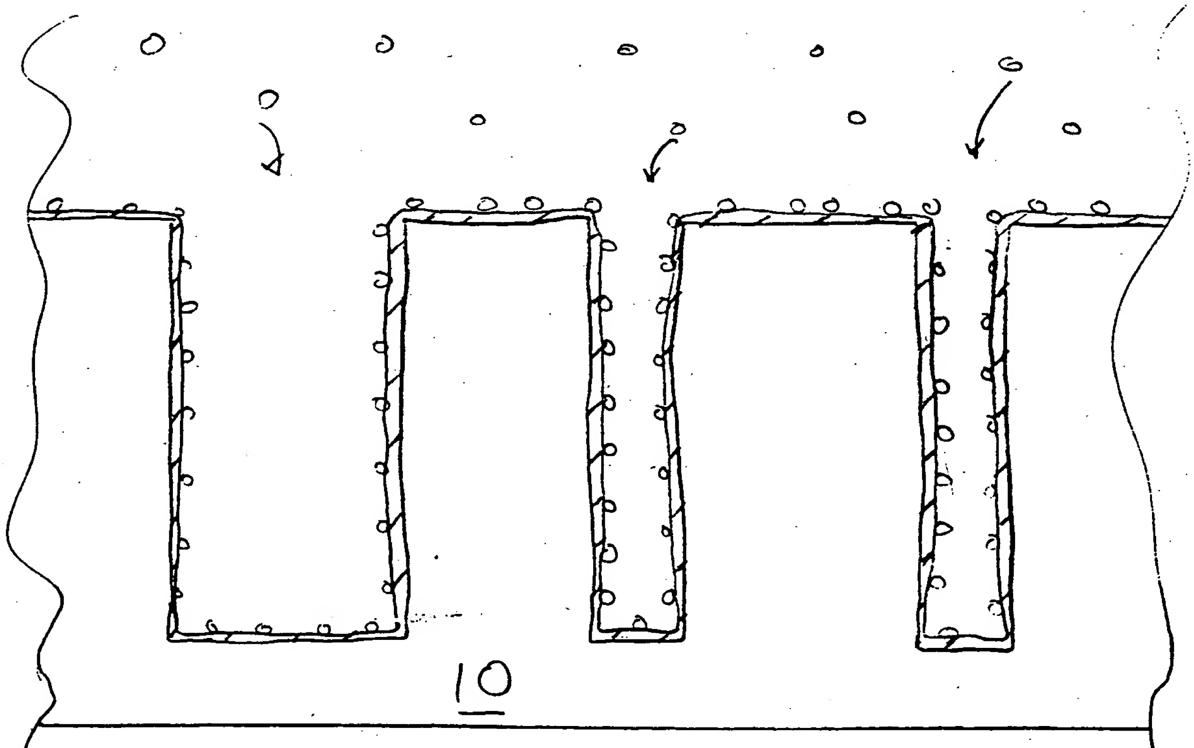


FIG. 8

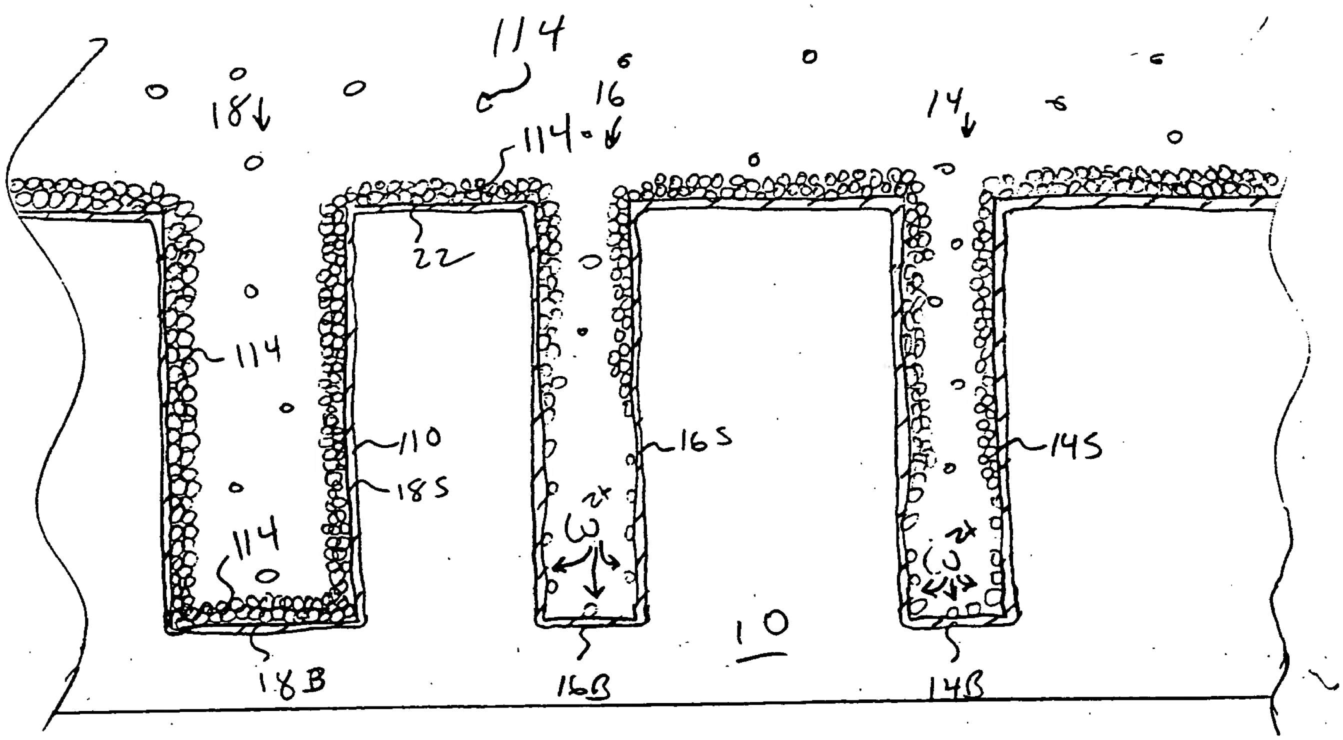
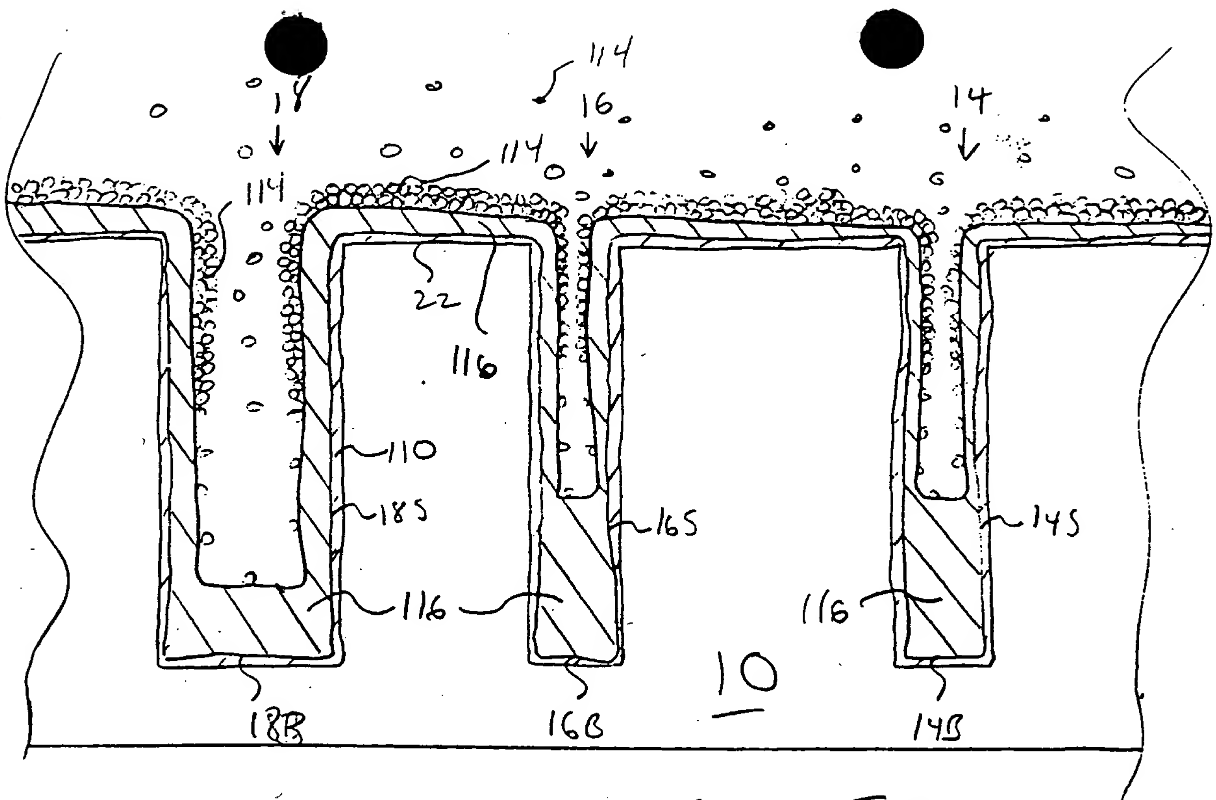


FIG. 9



18
114
16
14
114
114
22
116
110
18S
16S
14S
116
116
116
10
18B
16B
14B

FIG. 10

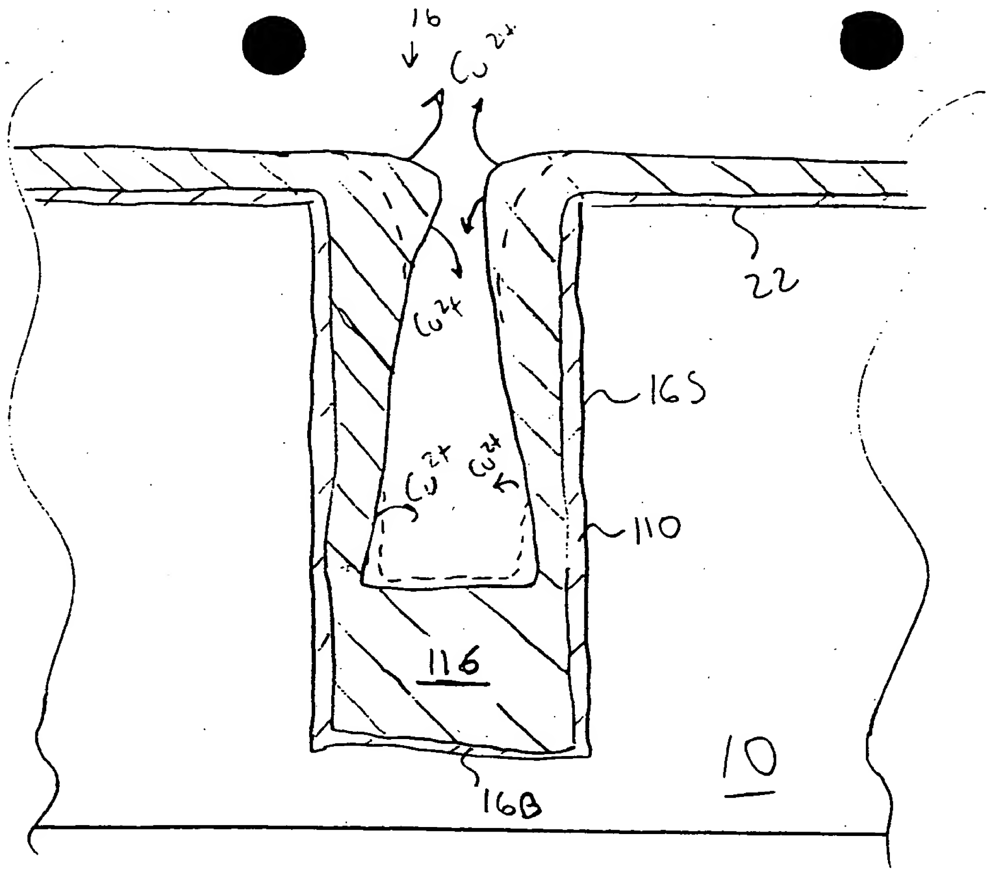

16
Cu2+
Cu2+
22
16S
Cu2+
Cu2+
Cu2+
110
116
10
16B

FIG. 12

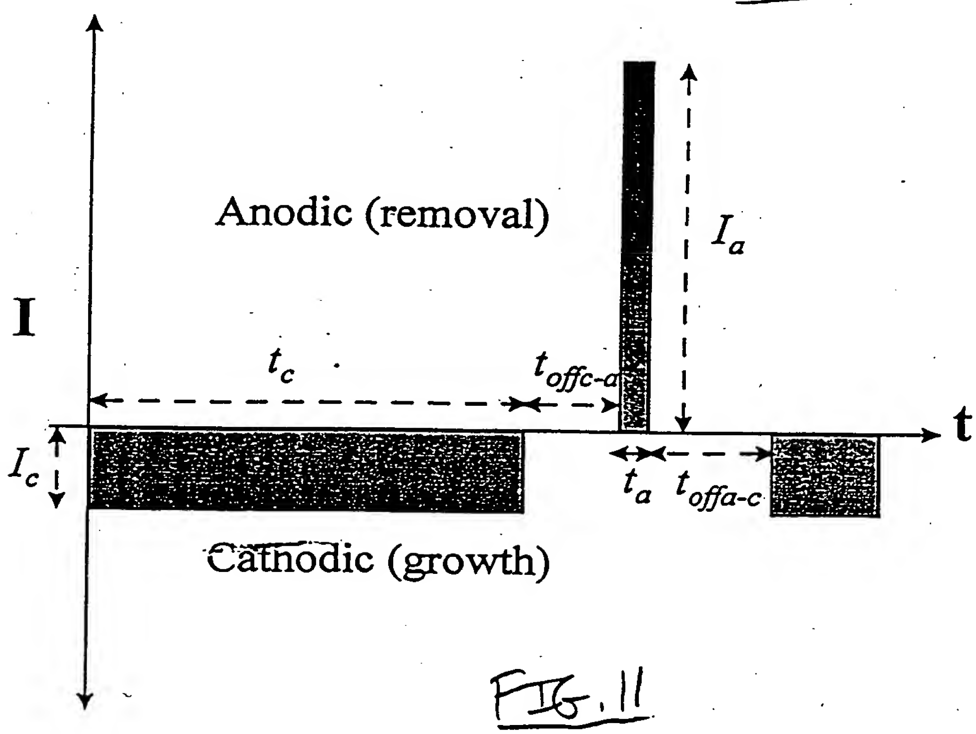
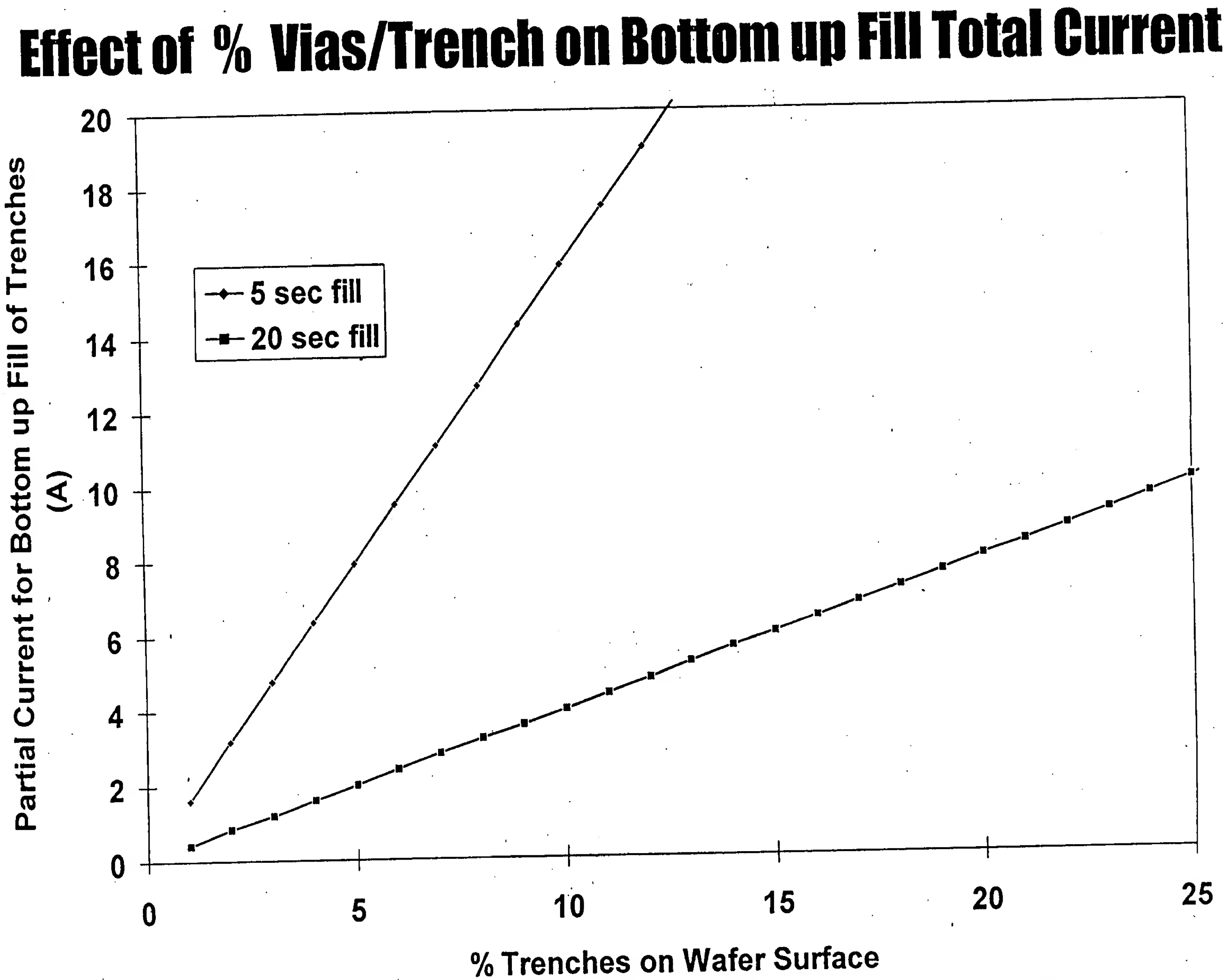

Anodic (removal)
I
I_a
t_c
t_{offc-a}
t
I_c
t_a
t_{offa-c}
Catnodic (growth)

FIG. 11

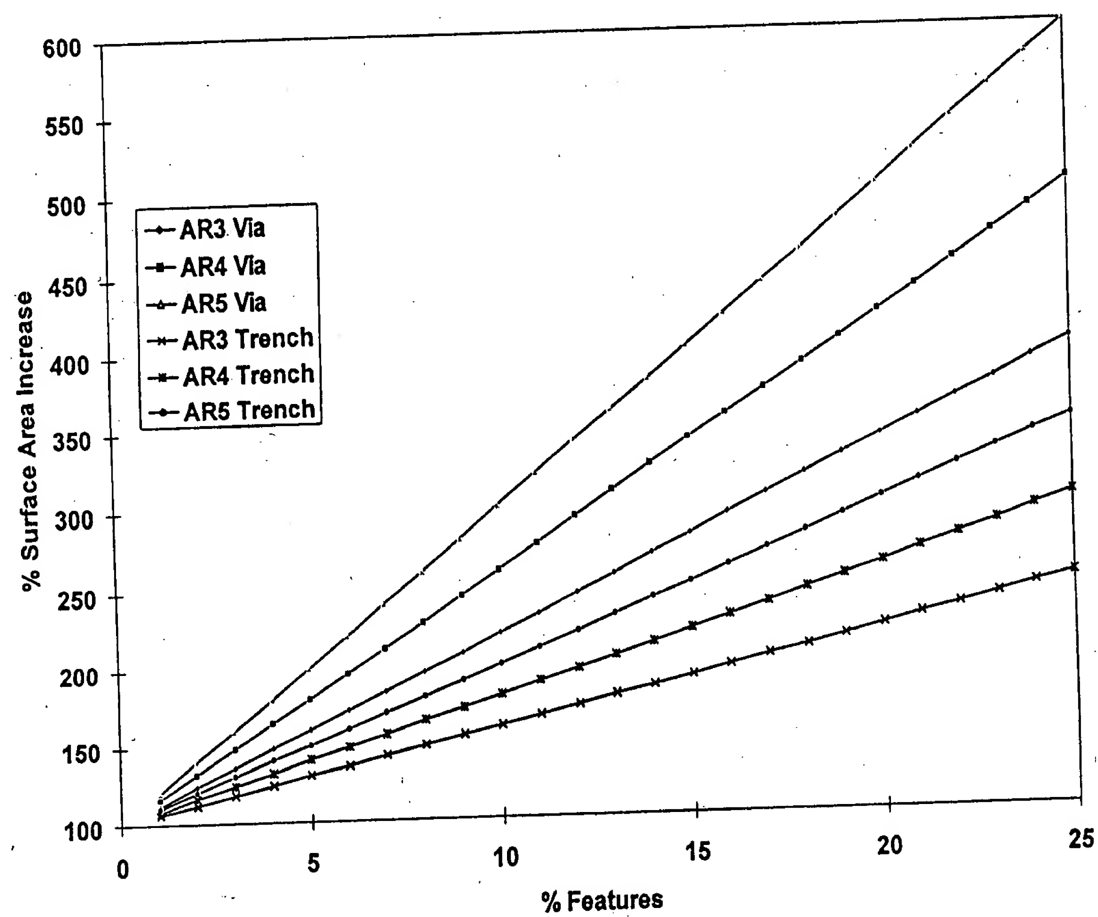
F I G. 13



Effect of % Vias/Trench on Bottom up Fill Total Current
Partial Current for Bottom up Fill of Trenches (A)
0
2
4
6
8
10
12
14
16
18
20
5 sec fill
20 sec fill
0
5
10
15
20
25
% Trenches on Wafer Surface

FIG. 14.

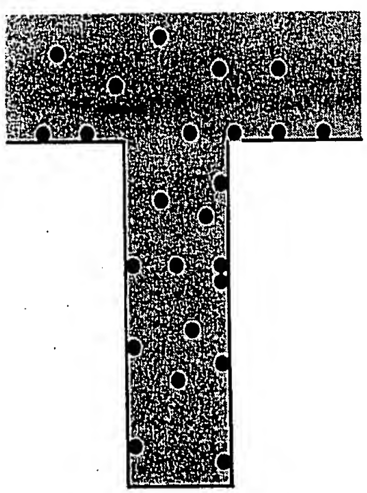
Surface Area With Features of Various Aspect Ratios



$$\frac{A_{total}}{A} = f_{field} + \sum_{i=1}^{n} f_i [1+4A] + \sum_{j=1}^{m} f_j [1+2A]$$

FIG. 15

How Much Additive Comes in With the Solution?



Ratio:

Surface to Solution Molecules

Aspect Ratio

2	299	60	155	52
2.5	365	73	190	63
3	432	86	224	75
3.5	498	100	259	86
4	565	113	293	98
4.5	631	126	327	109
5	697	139	362	121
5.5	764	153	396	132

Conditions

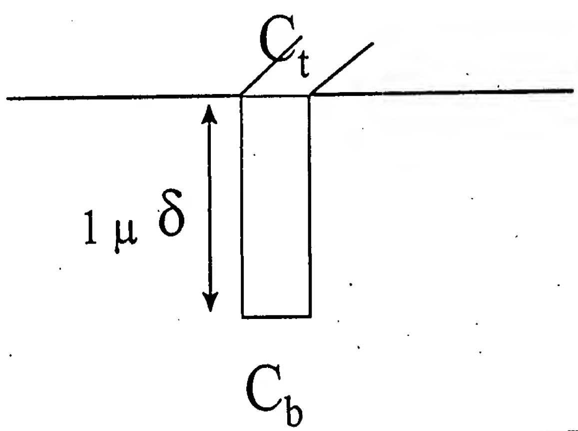
ppm	20	100	100	300
Mn	100	100	3000	3000
Moles/u^3	2.0E-19	1.0E-18	3.3E-20	1E-19
Molec/u^3	120460	602300	20077	60230
Molecules size (nm)	0.5	0.5	1.7	1.7
Molec/u^2	4000000	4000000	346021	346020.8

Conclusion: At all expected additive condition, there is insuffcent material stored in the inital solution within the via to lead to substantial surface absorption in the via.

-There will be an absorption time delay.

FIG. 16

Time Estimate for Plating Additives Absorption



Assumptions

1. Inital surface coverage is zero
2. Final surface coverage is $1x10^{15}$ molecules/cm^2 (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. No side wall absorption

$$\Delta C = 10\,ppm = 5.5x10^{-8}\ M/cm^3$$

$$\delta = 1\mu = 1.0x10^{-4}\ cm$$

$$D = 1.0x10^{-6}\ cm^2/\sec$$

Conclusions

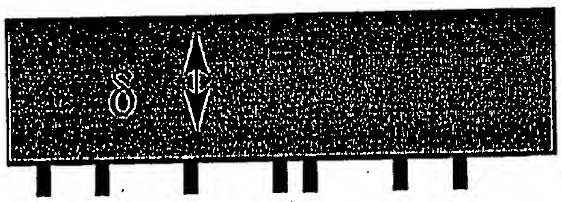
1. Diffusion controled absorption inside of trench take a few seconds.
2. Larger surface area of trench will increase this time from this estmate.
3. High additive level will decrease time estimate

$$F = \frac{D\Delta C}{\delta} = 5x10^{-10}\ M/\sec cm^2 = 3.4x10^{14}\,molecules/\sec cm^2$$

$$t_{abs} = 1x10^{-15}\,molecules/cm^2 / 3.4x10^{14}\,molecules/\sec cm^2 = 2.9\sec$$

FIG. 17

Time Estimate for Absorption of Plating Additives



Assumptions

1. Inital surface coverage is zero everywhere
2. Final surface coverage is $1x10^{15}$ molecules/cm^2 (1 monolayer).
3. Very fast absorption kinetics (diffusion controlled)
4. Concentraton at edge of boundary layer is bulk

$$\Delta C = 10\,ppm = 5.5x10^{-8}\ M/cm^3$$

$$\delta = 5.7\,\mu = 5.7x10^{-4}\ cm$$

$$D = 1.0x10^{-6}\ cm^2/\sec$$

Conclusions

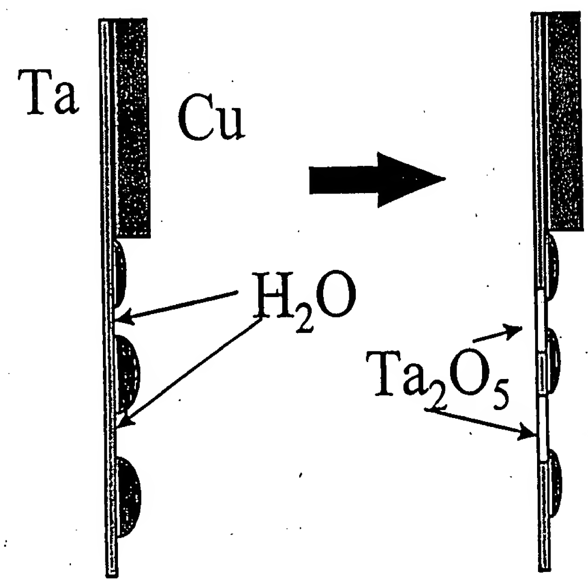
Diffusion of very low concentration plating additives may take several seconds to occur

$$F = \frac{D\Delta C}{\delta} = 1x10^{-10}\ M/\sec cm^2 = 0.7x10^{14}\,molecules/\sec cm^2$$

$$t_{abs} = 1x10^{-15}\,molecules/cm^2 / 0.7x10^{14}\,molecules/\sec cm^2 = 14\sec$$

F16.18

How Would Ta_2O_5 be Formed in the Side Walls?

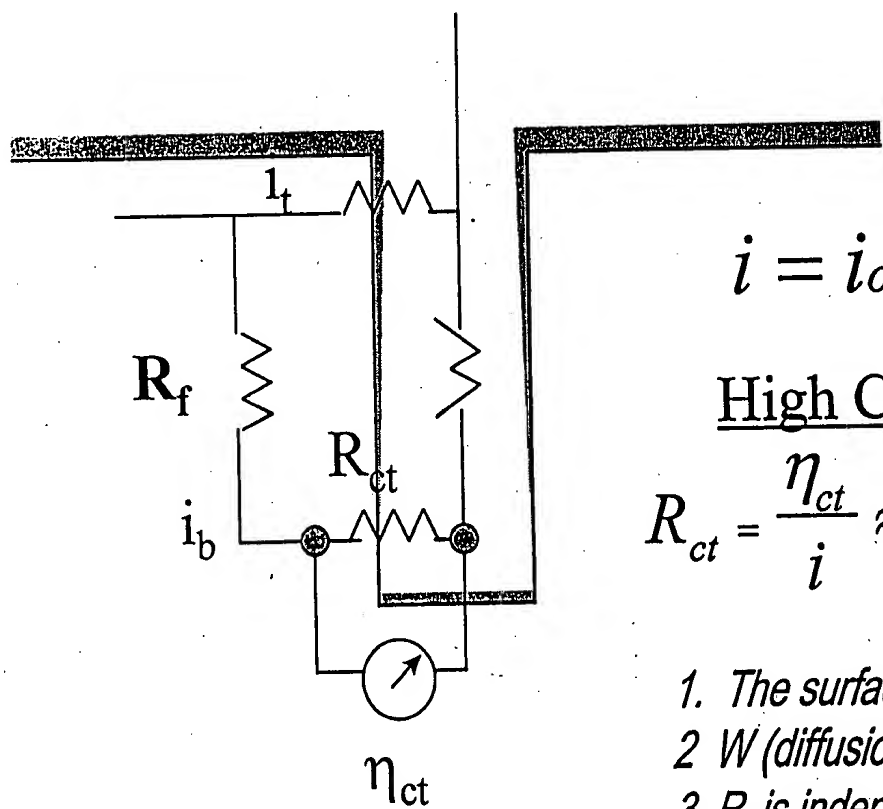


$$
\begin{array}{lll}
2Ta + 5H_2O & Ta_2O_5 + 10H^+ + 10\,e^- & E_o = -0.75V \\
10\,H^+ + 10\,e^- & 5H_2 & E_o = 0.00\ V \\
\hline
2Ta + 5H_2O & Ta_2O_5 + 5H_2 & \Delta E = 0.75V
\end{array}
$$

Conclusions: Formation of Ta_2O_5 is anticipated (thermodynamics)'

FIG. 19

Equivalent Circuit Model of Via/Trench Filling



$$i = i_o\left[e^{-\alpha n f \eta_{ct}} - e^{(1-\alpha) n f \eta_{ct}}\right]$$

<u>High Current</u>

$$R_{ct} = \frac{\eta_{ct}}{i} \approx \frac{\eta_{ct}}{i_o\, e^{-\alpha n f \eta_{ct}}}$$

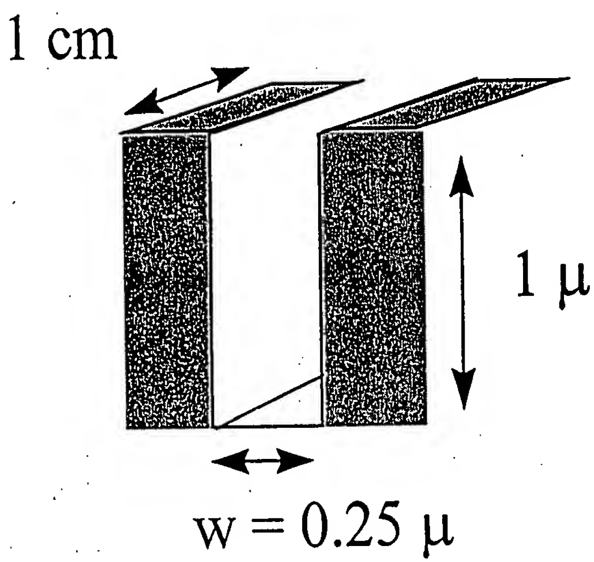
<u>Low Current</u>

$$R_{ct} = \frac{\eta_{ct}}{i} \approx \frac{1}{i_o n F}$$

1. The surface resistance increases with decreasing current !
2 W (diffusion resistance) increases with increasing current
3. R_f is independant of current

FIG. 20

Electrical Resistances and Filling of Small Features



$$R = \frac{\rho L}{2A} = 4\,m\Omega, 50\,k\Omega$$

$$\Delta V = IR = (iw)R$$

ΔV_{Ta} = 1x10^{-9} to 5x10^{-6} V

ΔV_{Ta2O5} = 0.003 to 0.16 V

Assumptions

1. Only Ta or TaO_2 (2 nm thick) is present on side wall for electrical conductivity
2. Plating occurs only at bottom of trench at 10-500 mA/cm^2 (conformal vs fast bottom-up fill rates).

$\rho_{T\alpha} = 16 \times 10^{-6}\ \Omega$ cm, $\rho_{T\alpha 2O5} = 50\ \Omega$ cm

Conclusions

1. If sidewall metallic Ta of 2 nm is present in the feature, electrical resistivity is insignificant.
2. If sidewall material is cracked, exposed to oxygen and converted to TaO_2, the electrical resistance in the film will be to large to support bottom-up filling.

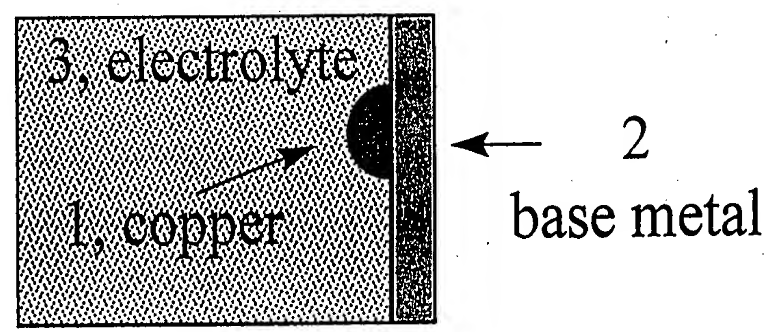
FIG. 21

Nucleation Phenomena

$$\Delta G_t = \pi r^2(2\sigma_{13} + \sigma_{12} - \sigma_{23}) + \frac{2}{3}\pi r^3 \Delta G_v$$

$$\frac{\Delta G_t}{v_m} = \frac{3\ (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2v_m r} + \Delta \overline{G}_v$$

$$E(r) = \frac{RT}{nF}\ln\left[\frac{3\ (2\sigma_{13} + \sigma_{12} - \sigma_{23})}{2v_m r} + \Delta G_v\right]$$



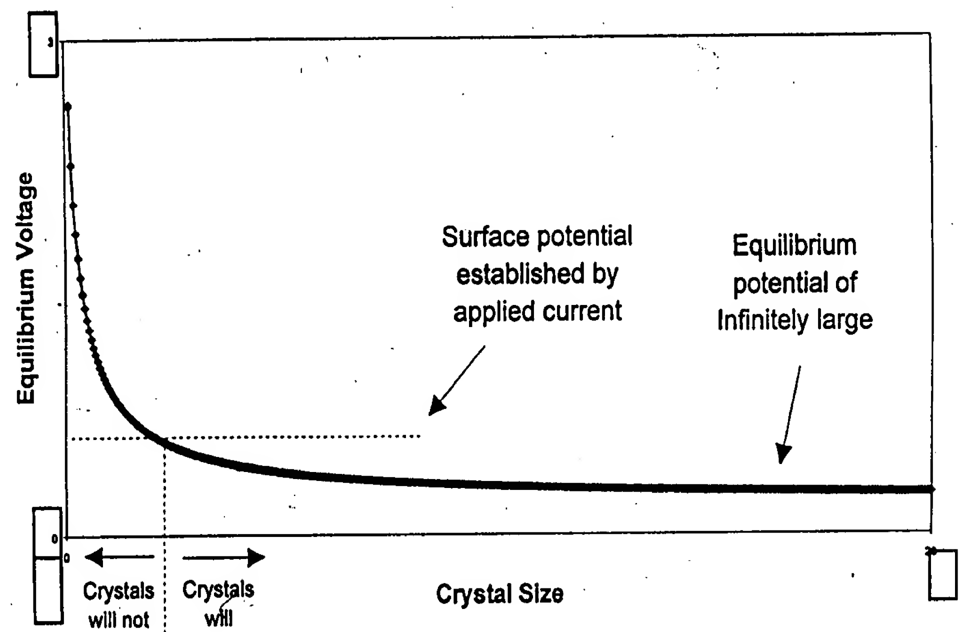
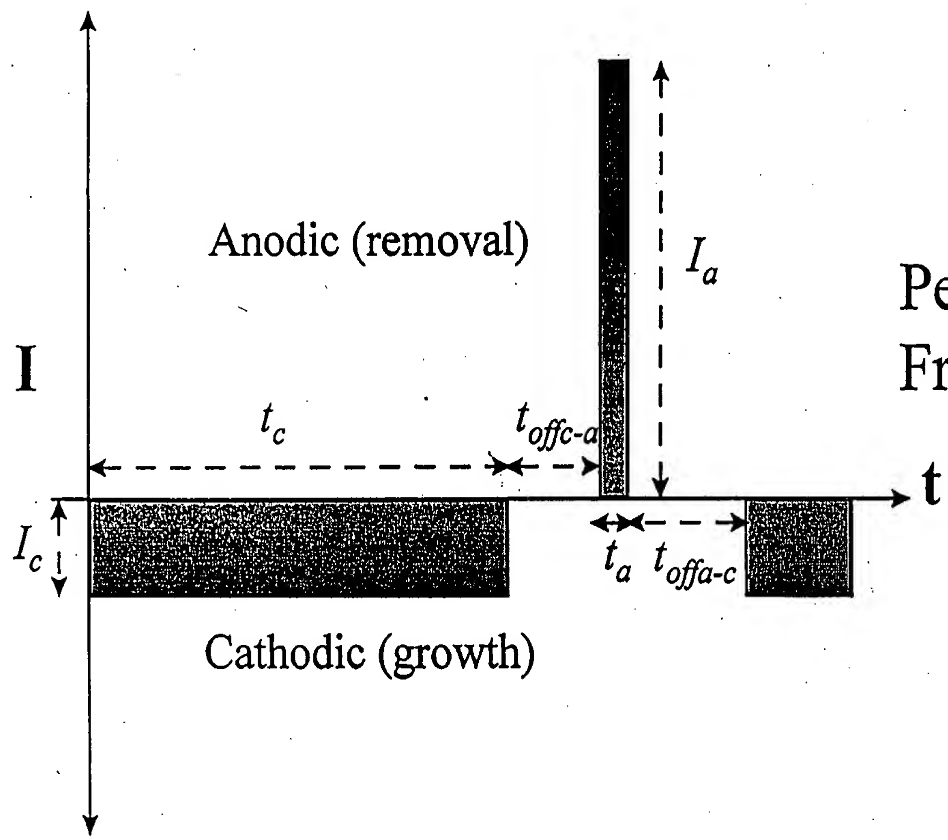


FIG. 22

Bipolar Pulse Plating Waveform



Period $= t_c + t_a + t_{offc\text{-}a} + t_{offa\text{-}c}$

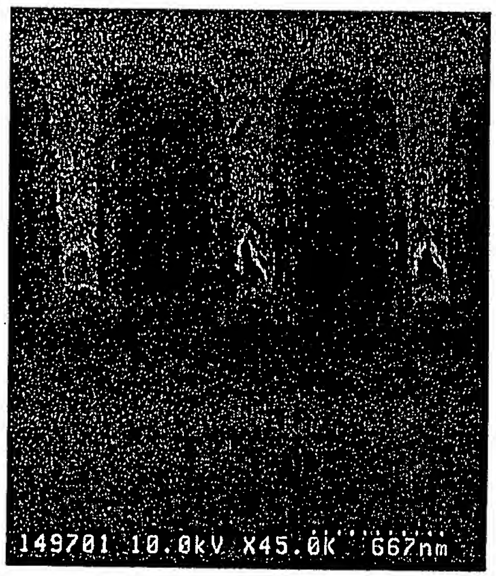
Frequency = 1/Period

Constraint: $I_c \cdot t_c - I_a \cdot t_a > 0$

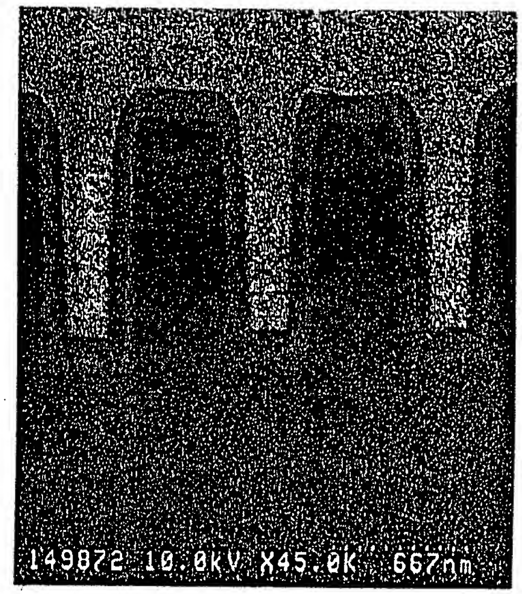
FIG. 23

Bipolar pulse plating: Phase 1-waveform screening

- Select tests
- Bipolar pulse with hi anodic current showed improvement over POR
- Eliminated other pulse waveforms



POR 1.0, 7A DC



10A Cathodic, 80 A Anodic, 125 Hz, 10 msec t_{off}

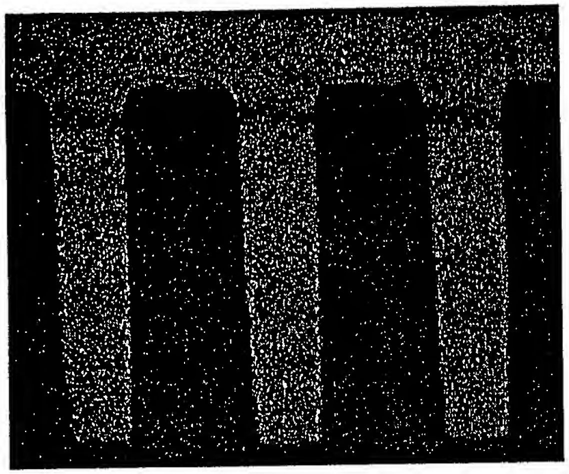
FIG. 24

Bipolar pulse plating: Phase 2-Trench optimization

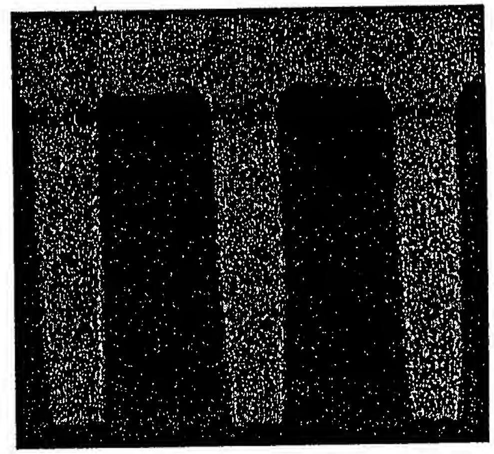
- 2 types of waveforms tested
- No pulsed waveform resulted in better fill than POR 1.0
- Higher pulsed anodic currents improved top filling
- Lower pulsed cathodic current improved filling
  - longer on-times were better

FIG. 25

Fill Improvement: Reverse pulse matrix

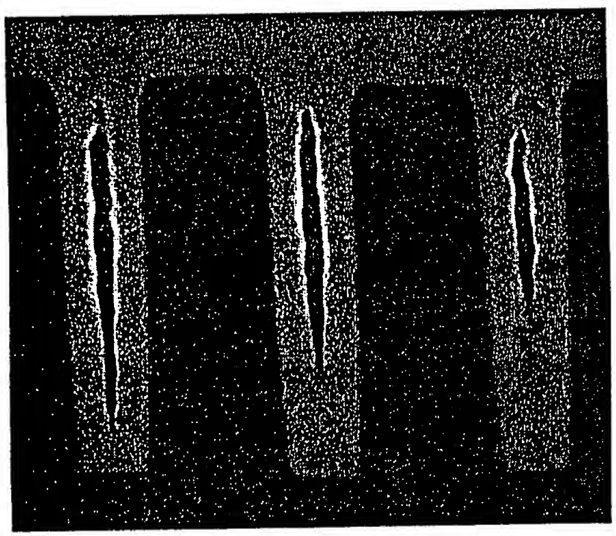


A



Field 5, 0.34 μm, AR = 4.5

B



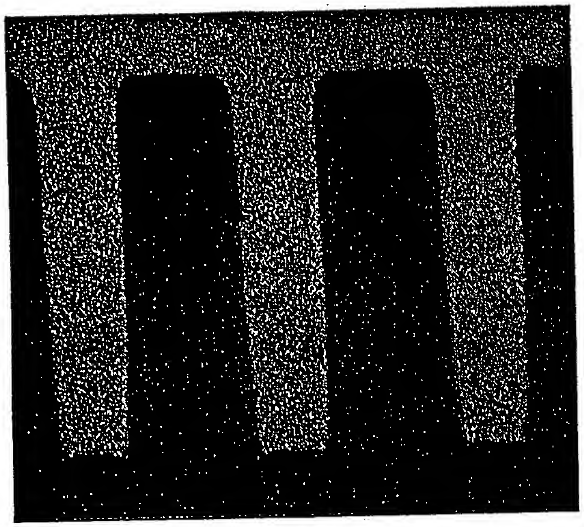
Control, 7A DC

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	25	10	*0*
B	4	25	10	*3*

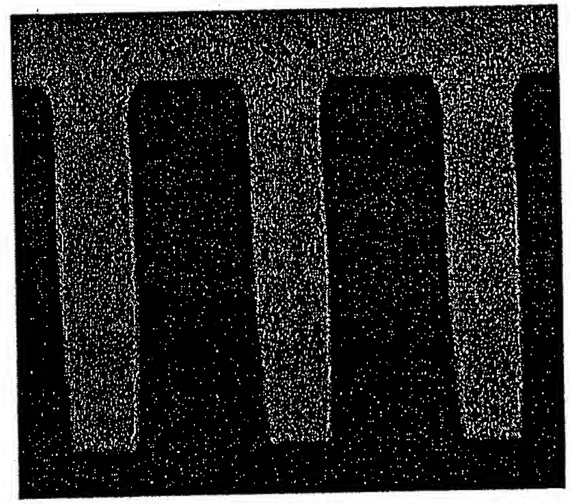
•*Feature*: SEMATECH Standard vias
•*Seed*: 1600Å HCM Cu/250Å HCM Ta
•*Plate*: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

FIG. 26

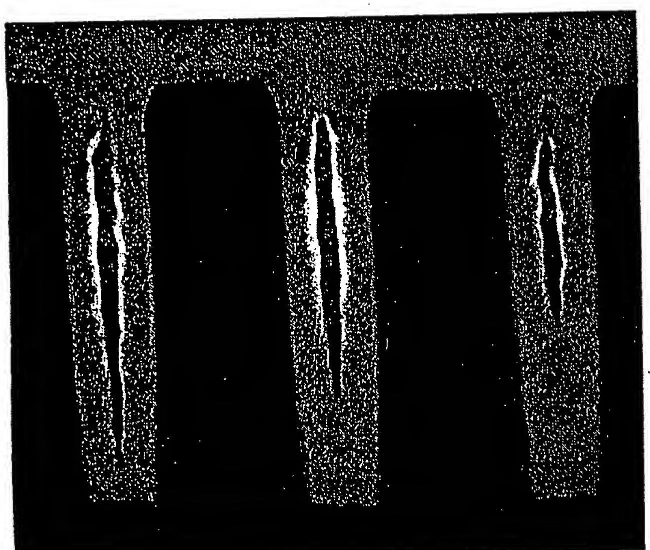
Fill Improvement: Reverse pulse matrix



A



B



Control, 7A DC

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	24	100	*0*
B	4	22	100	*3*

•*Feature*: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5

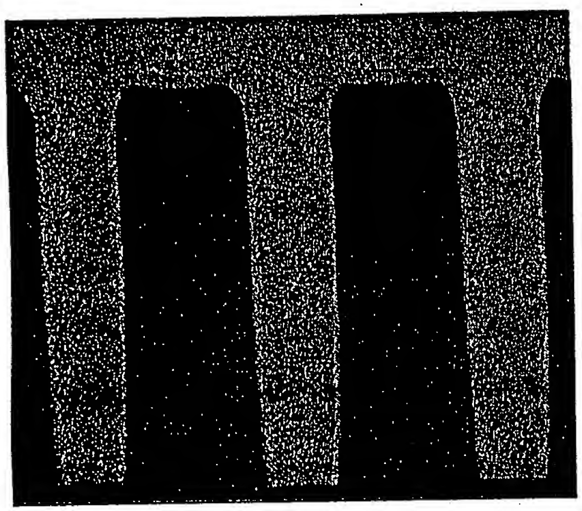
•*Seed*: 1600Å HCM Cu/250Å HCM Ta

•*Plate*: Step 1: 0.25A DC, 50 sec

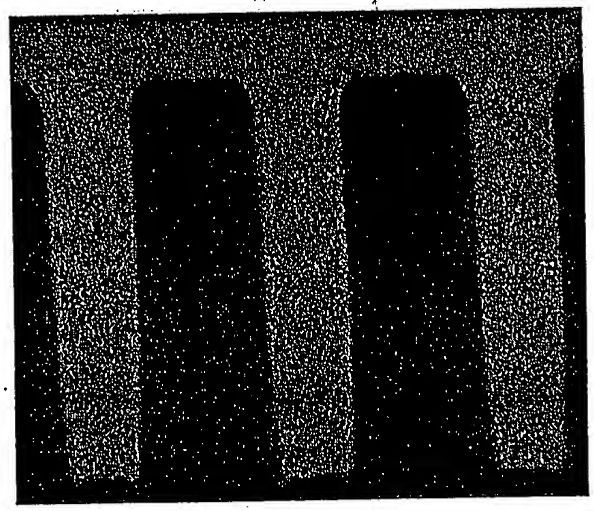
Step 2: Pulse

FIG. 27

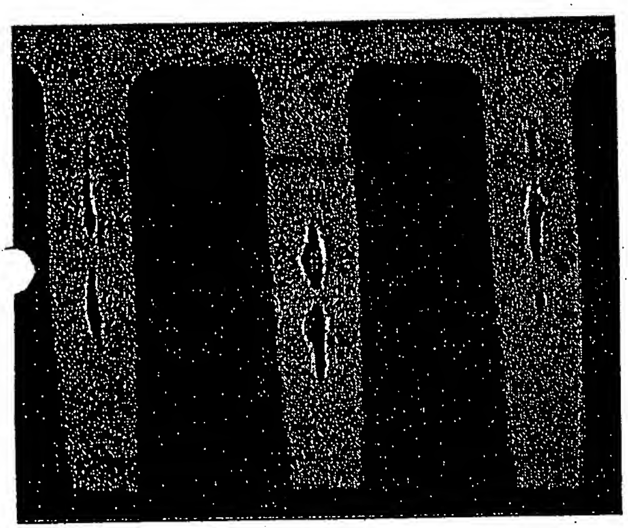
Reverse pulse matrix: Impact of t_c/t_a ratio/freq.



A



B



C

D

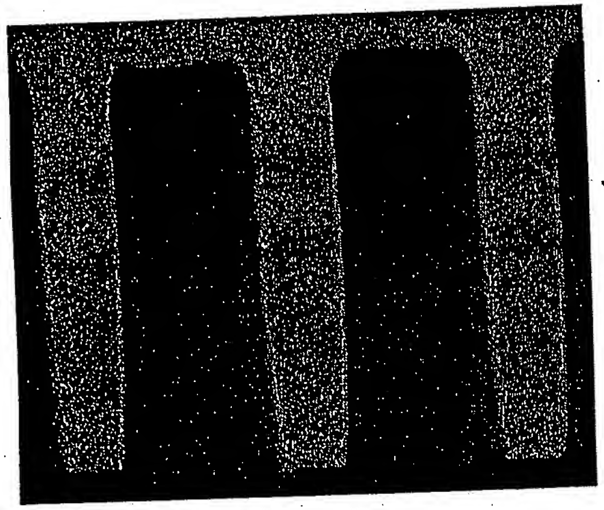
- ***Feature***: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5
- ***Seed***: 1600Å HCM Cu/250Å HCM Ta
- ***Plate***: Step 1: 0.25A DC, 50 sec
  Step 2: Pulse

Pulse Matrix

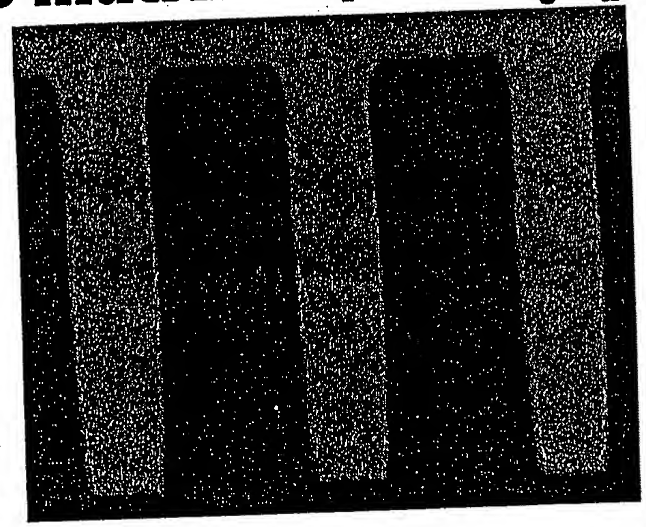
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	*25*	*10*	0
B	4	*25*	*100*	0
C	4	*49*	*10*	0
D	4	*49*	*100*	0

FIG. 28

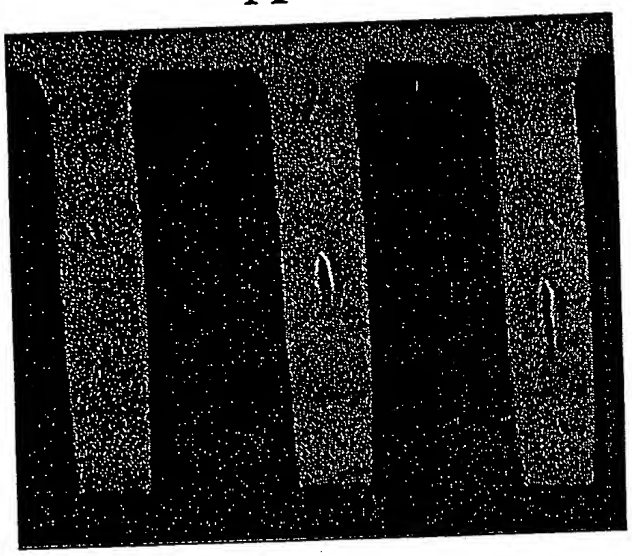
Reverse pulse matrix: Impact of t_c/t_a ratio/freq.



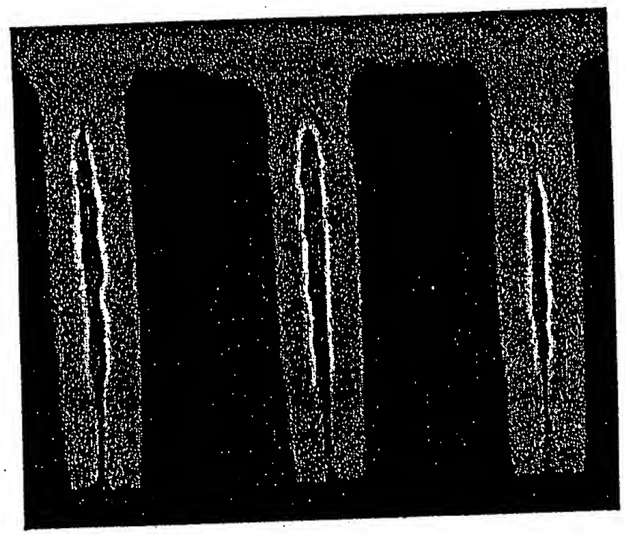
A



B



C



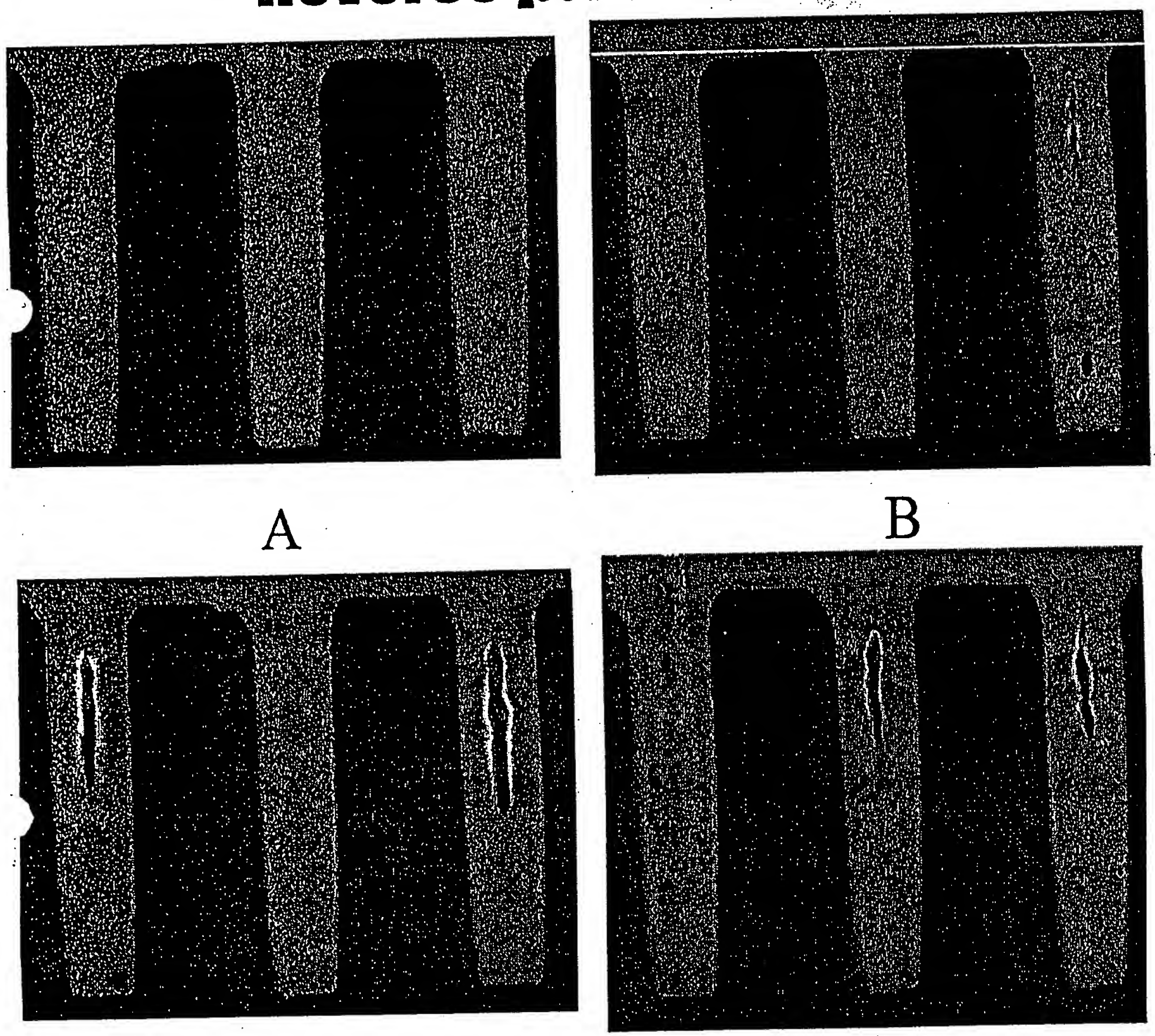
D

- ***Feature***: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5
- ***Seed***: 1600Å HCM Cu/250Å HCM Ta
- ***Plate***: Step 1: 0.25A DC, 50 sec
  Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	*25*	*10*	3
B	4	*25*	*100*	3
C	4	*49*	*10*	3
D	4	*49*	*100*	3

FIG. 29

Reverse pulse matrix: Impact of t_c/t_a ratio



A B

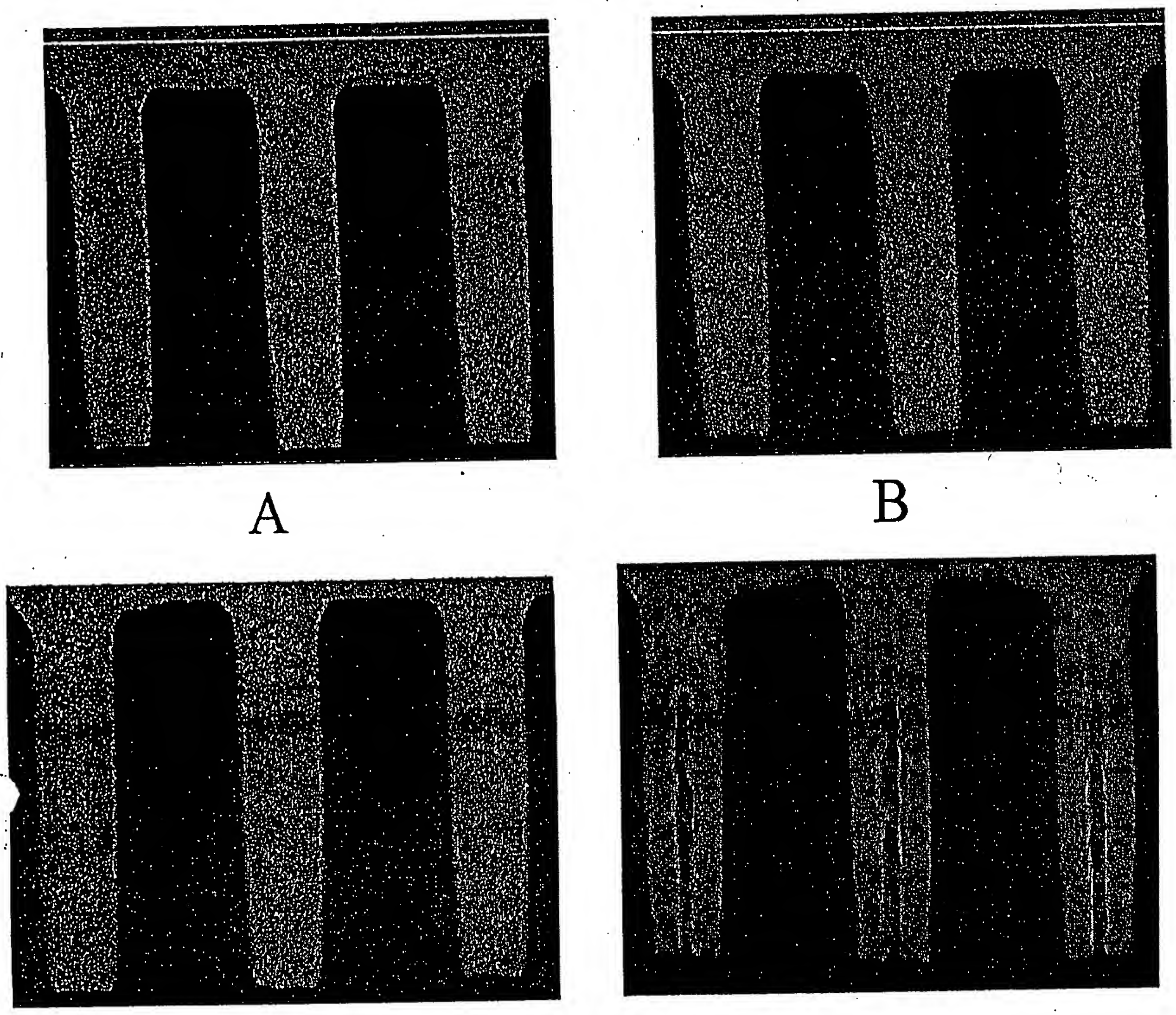
C D

•*Feature*: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5
•*Seed*: 1600Å HCM Cu/250Å HCM Ta
•*Plate*: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
C	8	*25*	10	*0*
D	8	*25*	10	*3*
C	8	*49*	10	*0*
D	8	*50*	10	*3*

FIG. 30

Reverse pulse matrix: Impact of cathodic current/freq.



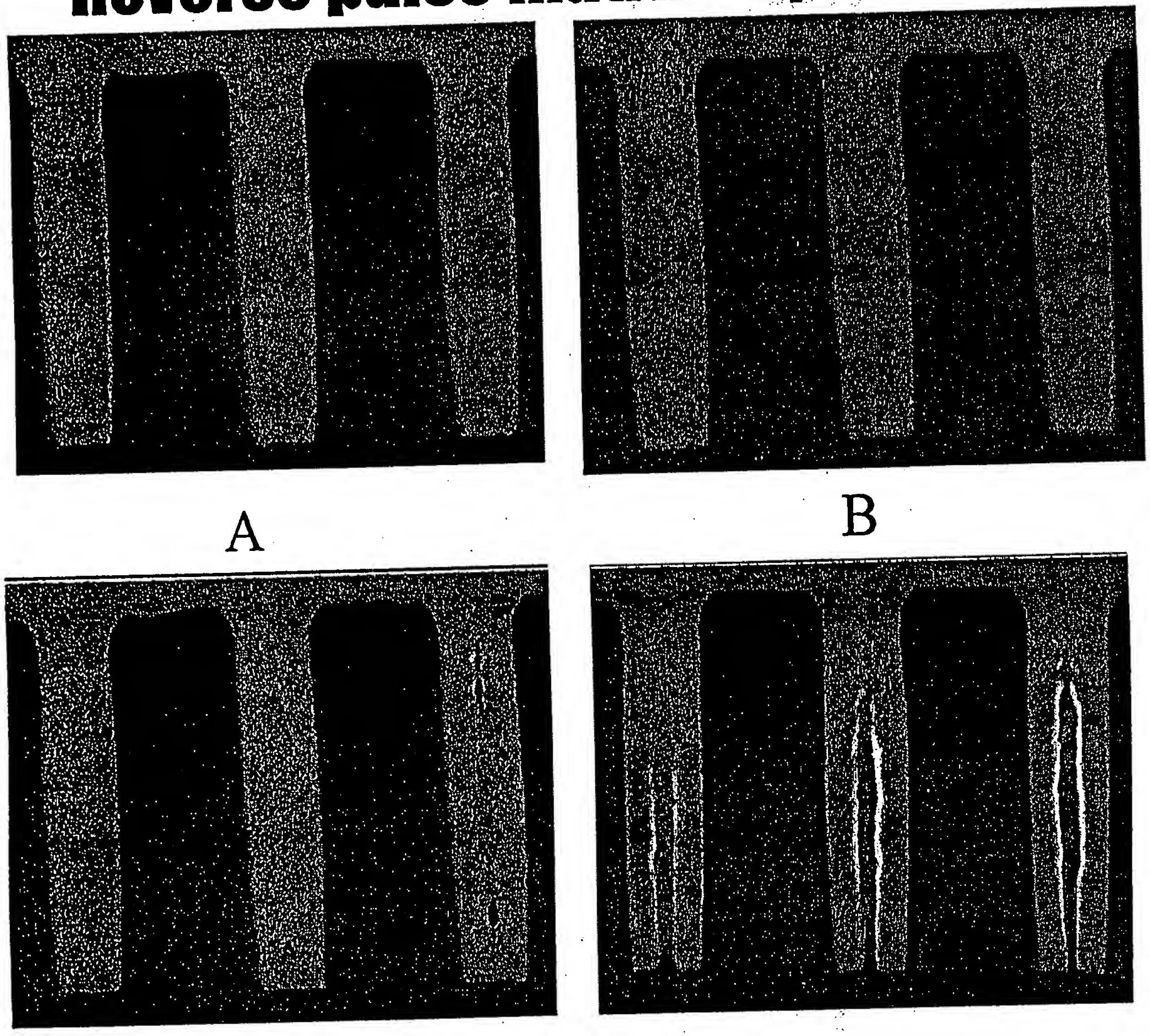
A B C D

- *Feature*: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5
- *Seed*: 1600Å HCM Cu/250Å HCM Ta
- *Plate*: Step 1: 0.25A DC, 50 sec
  Step 2: Pulse

Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	*4*	25	*10*	0
B	*4*	25	*100*	0
C	*8*	25	*10*	0
D	*8*	25	*100*	0

FIG. 31

Reverse pulse matrix: Impact of cathodic current/freq.



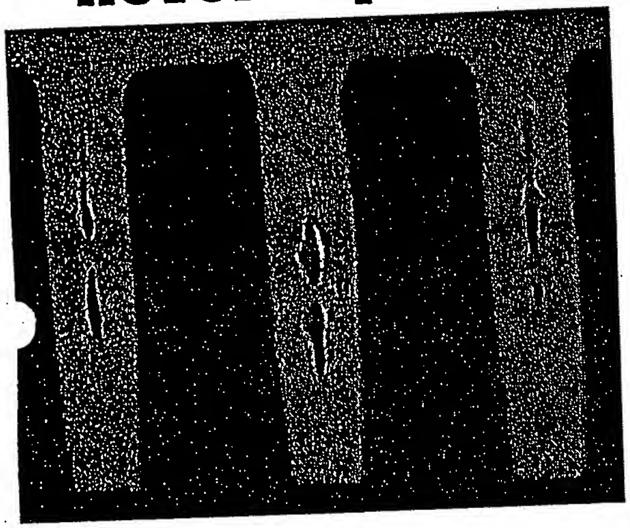
A B C D

•*Feature*: SEMATECH Standard vias, Field 5, 0.34 μm, AR = 4.5
•*Seed*: 1600Å HCM Cu/250Å HCM Ta
•*Plate*: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

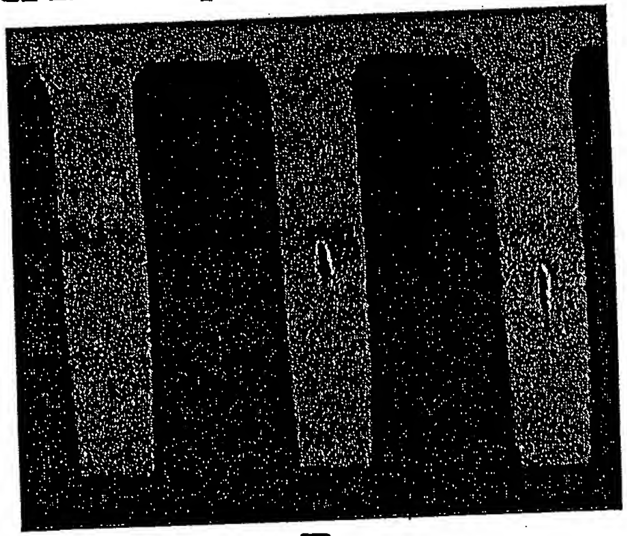
Pulse Matrix				
#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	*4*	25	*10*	3
B	*4*	25	*100*	3
C	*8*	25	*10*	3
D	*8*	25	*100*	3

FIG. 32

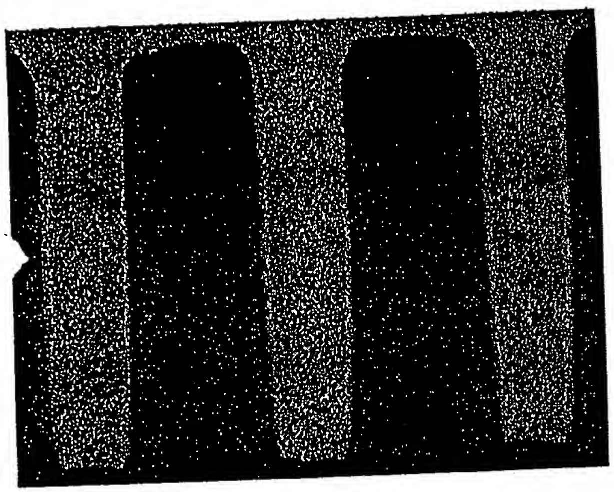
Reverse pulse matrix: Impact of cathodic current/off time



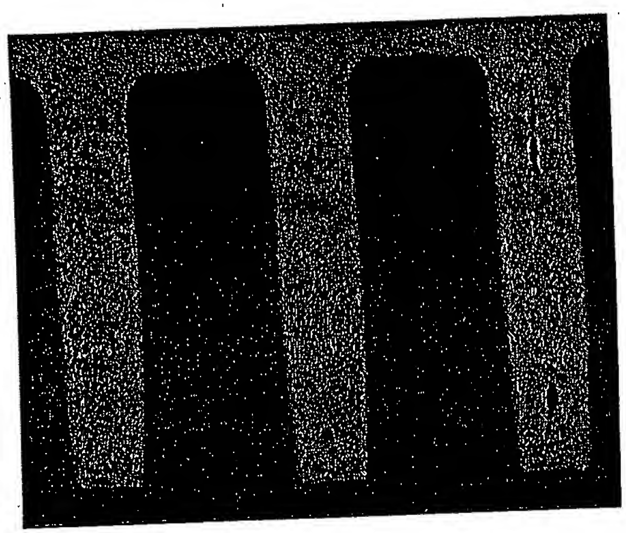
A



B



C



D

•*Feature*: SEMATECH Standard vias, Field 5, 0.34 µm, AR = 4.5
•*Seed*: 1600Å HCM Cu/250Å HCM Ta
•*Plate*: Step 1: 0.25A DC, 50 sec
Step 2: Pulse

Pulse Matrix

#	Ic	t_c/t_a ratio	Freq (Hz)	Toff
A	4	49	10	0
B	4	49	10	3
C	8	25	10	0
D	8	25	10	3

FIG. 33

Reverse pulse matrix:

- Reverse pulse shows superior fill compared to DC alone
  - Low current initiation <u>necessary</u>
  - Smallest features filled (0.34 μm, 4.5 AR)
- Initial data indicates longer reverse pulse time yields better fill
- 100 Hz clearly shows poorer fill than 10 Hz
- 5:1 AR Via structure breakpoint
  - Initiation limit-cannot overcome seed deficiency
  - Observed in backfilled via fill (Field 4, 0.21 μm, 5:1 AR) also

Center voids eliminated on wafer edge and center by reverse pulse plating

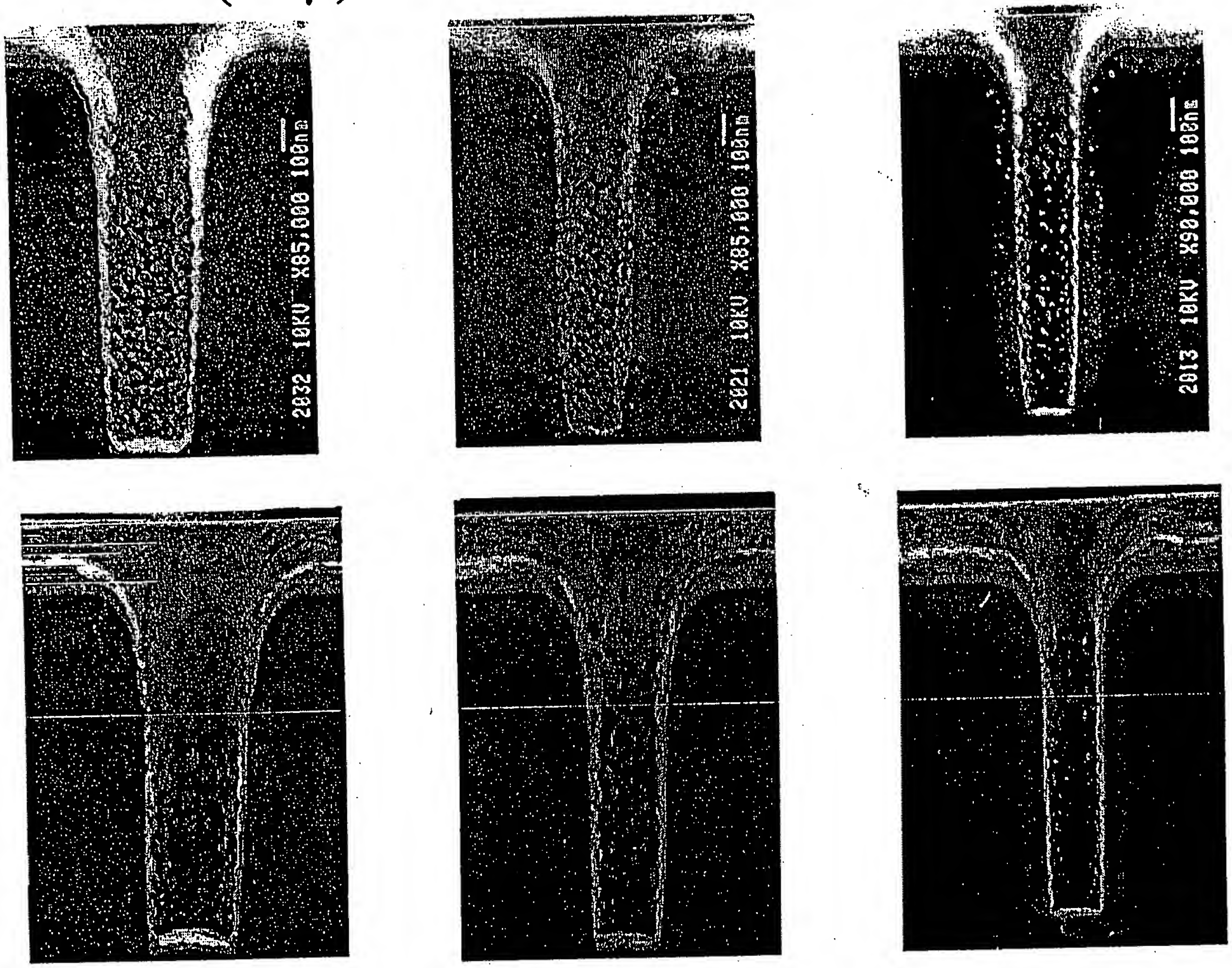
FIG. 34

HCM vs. IMP Seed Comparison on Backfilled Vias

Field 1(.30μ) Field 3(.25μ) Field 4(.21μ)

IMP

HCM POR6



Note: 300 Å Ta + 2400 Å Cu

FIG. 35

Current Sweep Experimental Matrix #1

Experiment Number	Initial Current (A)	Maximum Current (A)	Time to Max Current (s)	Time at Max Current (s)	Current Sweep (mA/sec)	Total Equiv. Deposition Thick (Å)
1	0.1	2	25	82	76	2511
2	0.1	4	75	9	52	2505
3	0.1	4	60	17	65	2521
4	0.1	2	60	64	32	2521
5	0.25	2	50	68	35	2538
6	0.25	4	90	0	42	2525
7	0.25	4	45	24	83	2529
8	0.25	2	90	45	19	2525

FIG. 36

Current Sweep Experimental Matrix #1

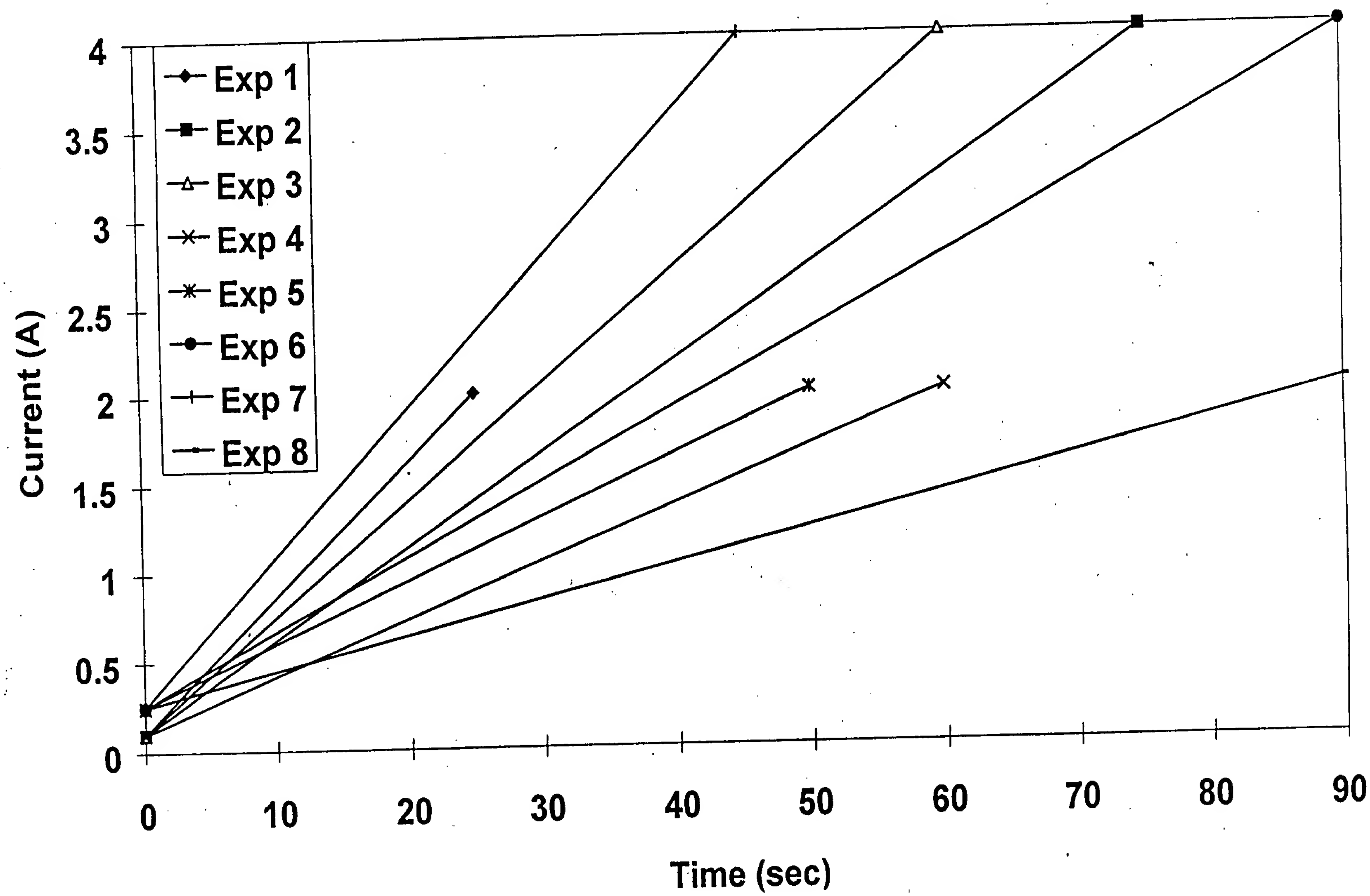


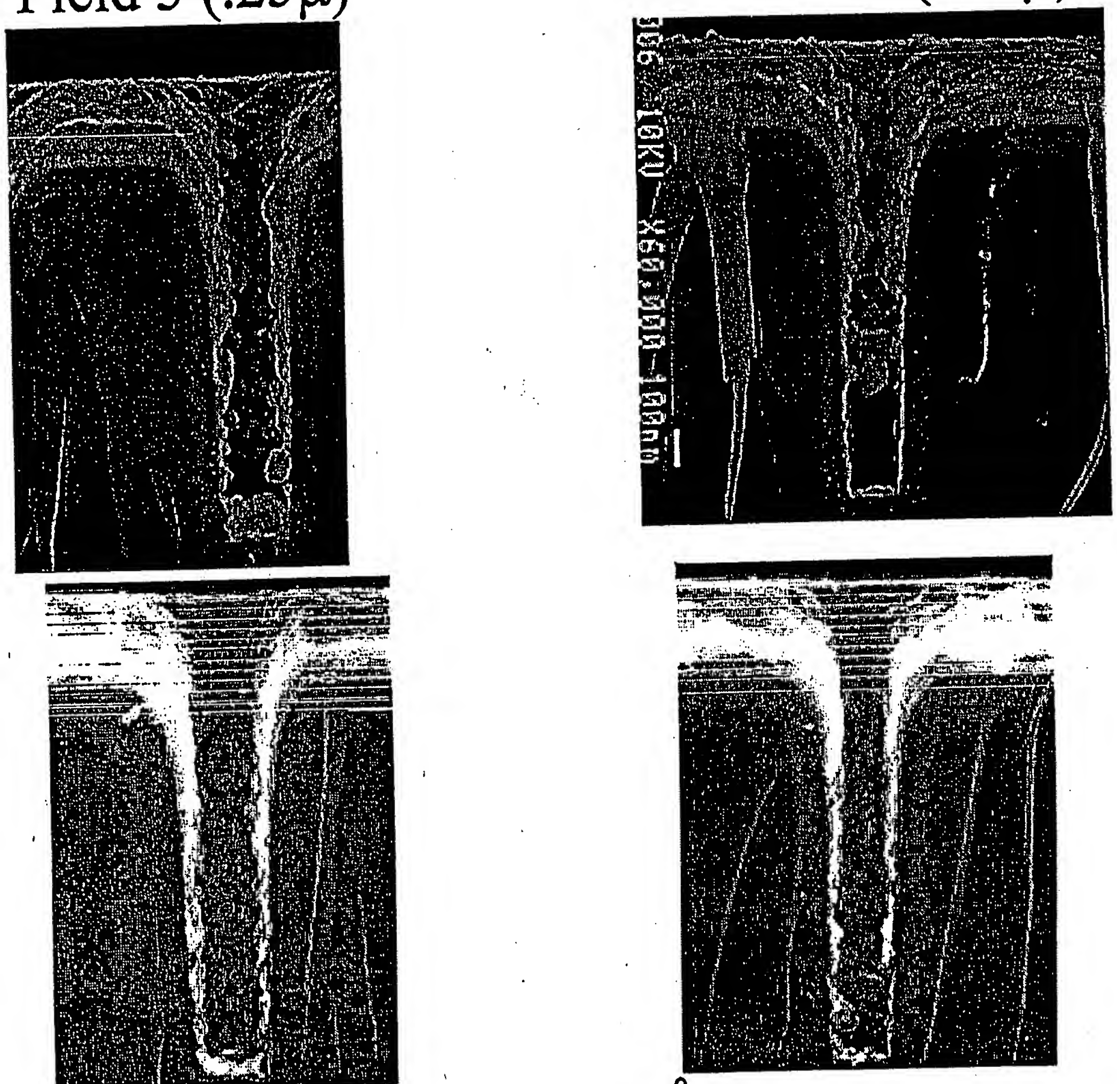
FIG. 37

Comparison: .5 Amp to .1 Amp Initiation

Field 3 (.25μ) Field 4 (.21μ)

.1 A
100s

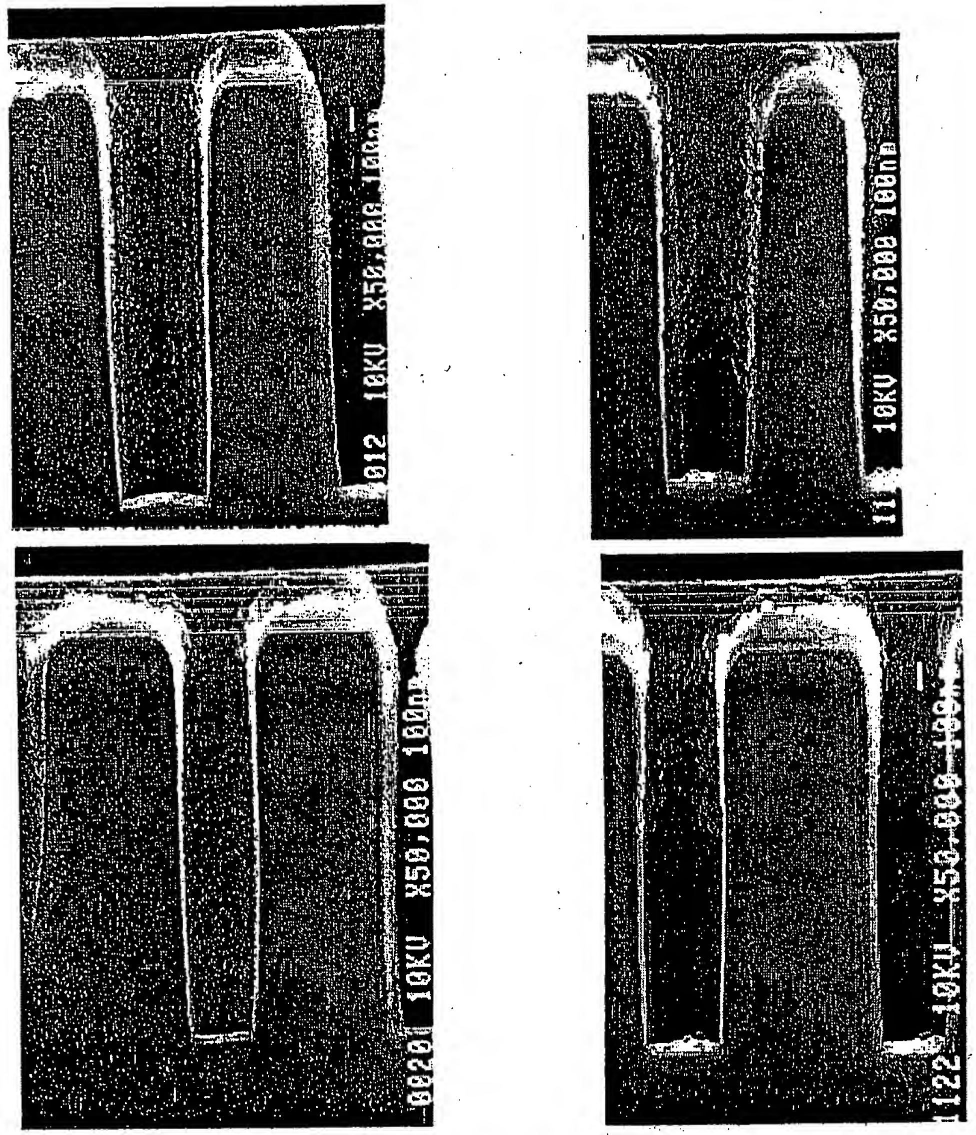
.5 A
22.5s



Note: HCM POR6, 300 Å Ta + 2400 Å Cu

FIG. 38

Impact of induction time



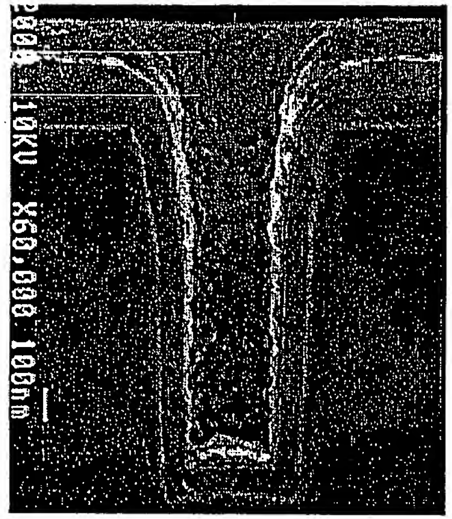
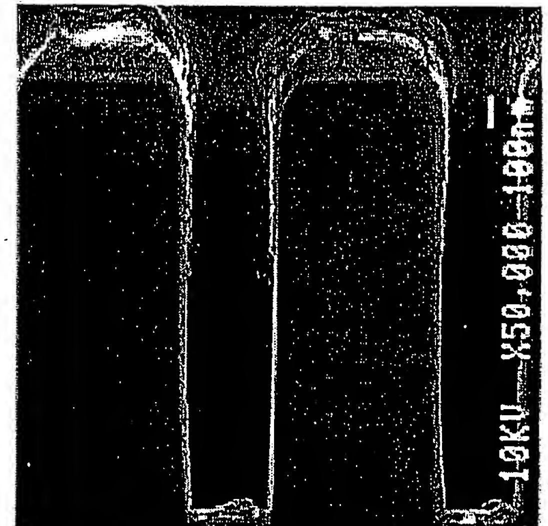
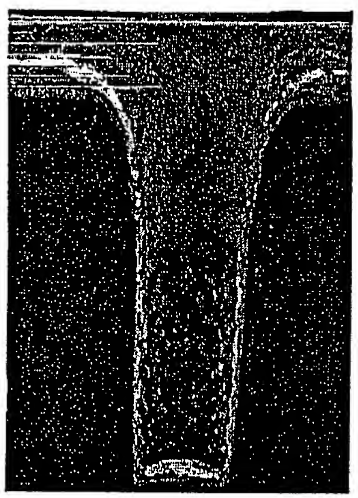
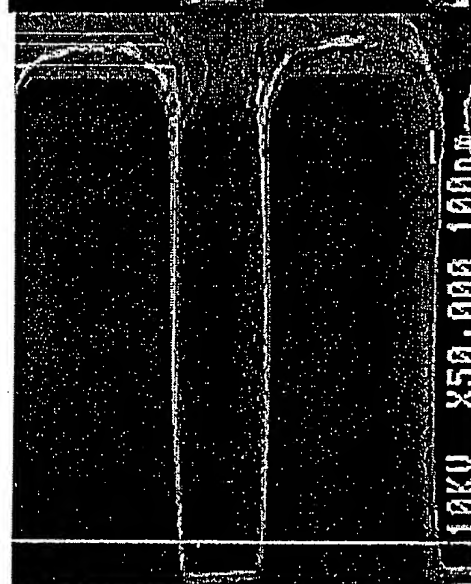
HCM
Cu/Ta
1600 Å Cu
/250 Å Ta

Conclusion

- *Induction removes critical seed layer*

FIG. 39

Induction Comparison: Backfilled vs. Non-Backfilled Vias

	Backfilled	Non-Backfilled
2 sec Ind.		
Seed Only		

Note: HCM POR6 seed (2000-2400 Å), .3μ wide

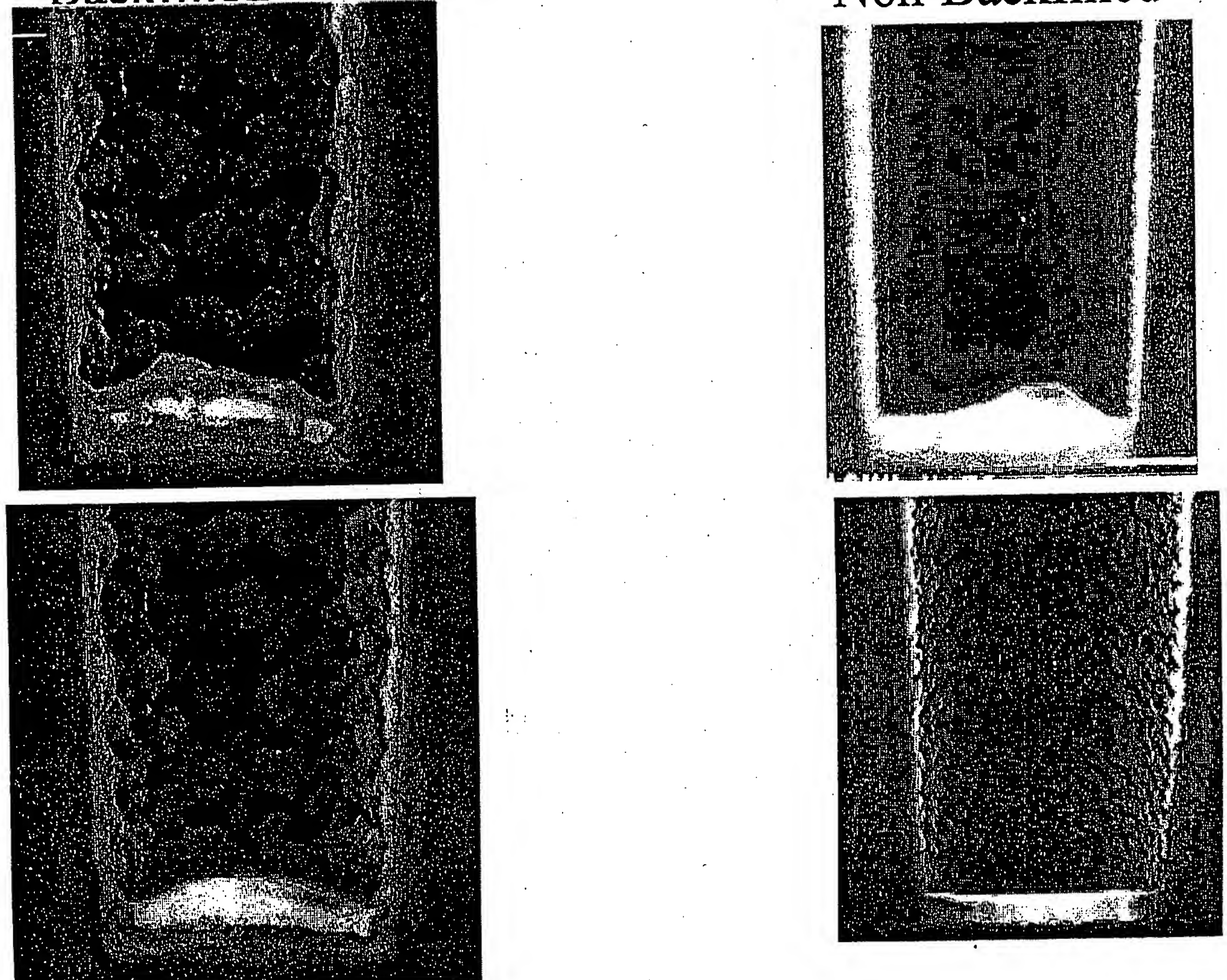
FIG. 40

Induction Comparison: Backfilled vs. Non-Backfilled Vias

Backfilled | Non-Backfilled

2 sec Ind.

Seed Only

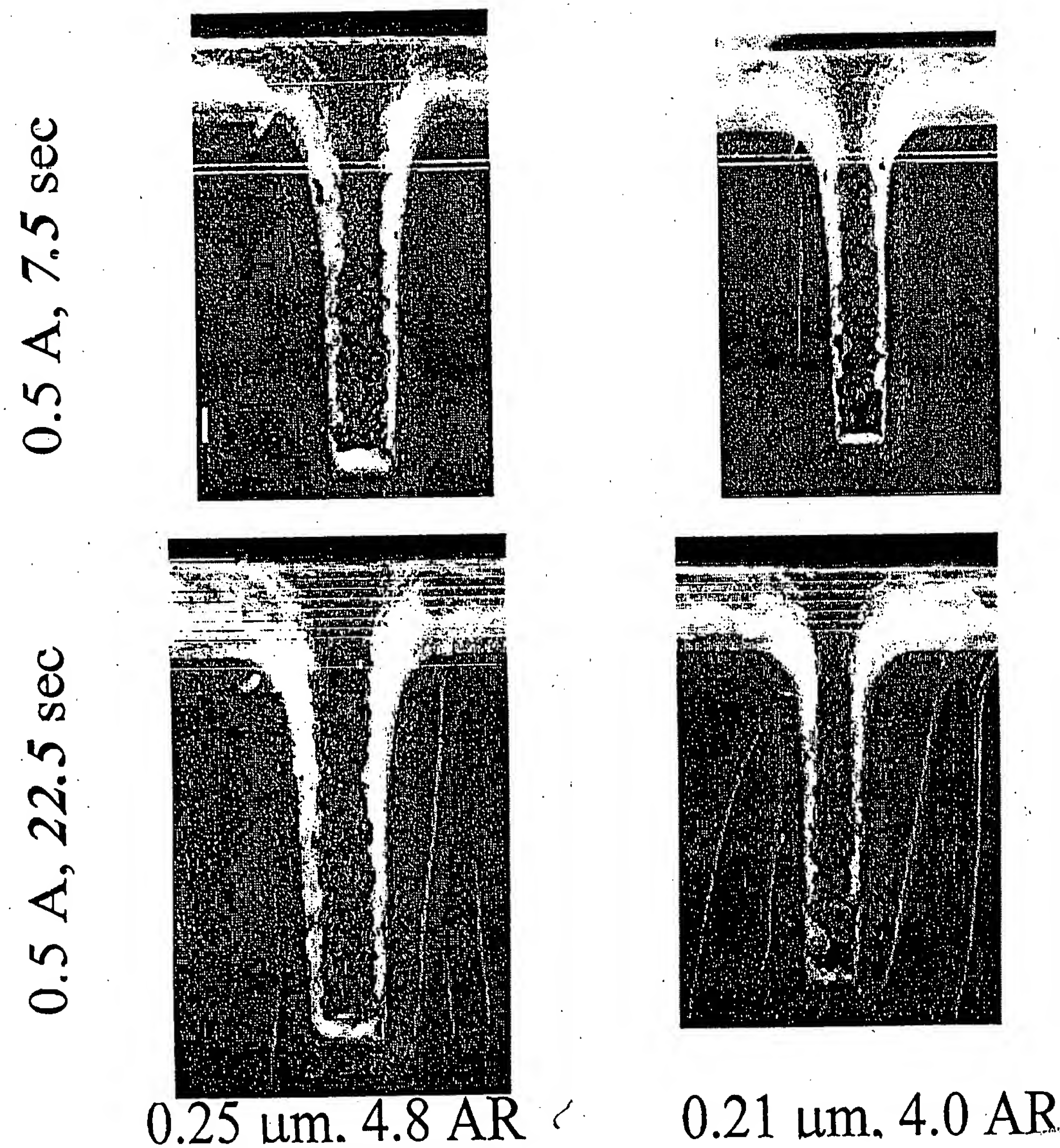


Note: HCM POR6 seed (2000-2400 Å), .3μ wide

009SFF77 9F09F260

FIG. 41

Initiation profile- Conformality



- HCM Cu/Ta
- 1600 Å Cu /250 Å Ta

Conclusion

- *Conformal growth even at small features*

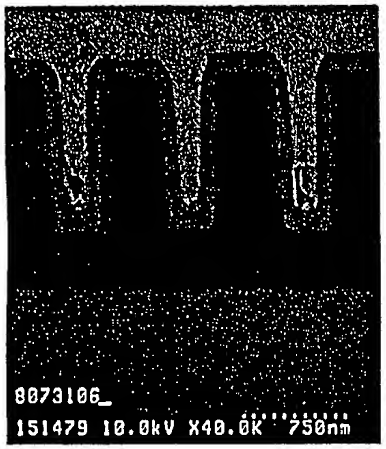
FIG. 42

Unipolar Pulse Tests: 0.18 μ Via Wafers

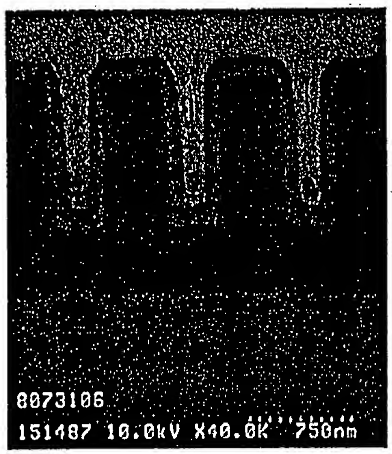
Wafer Id	Seed Thick	Induction Time	Initiation Time	Initation Conditions	Fill Time	Fill Current
3106-03	1600 Å	O seconds	8 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-04	1600 Å	O seconds	8 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-05	1600 Å	O seconds	16 seconds	5% 20 A 0.5A DC	15 seconds	7 A
3106-06	1600 Å	O seconds	16 seconds	2%, 50A 0.5A DC	15 seconds	7 A
3106-08	1600 Å	O seconds	16 seconds	5% 20 A	15 seconds	7 A

FIG. 43

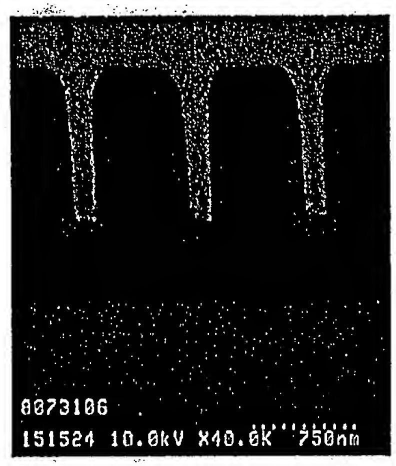
Unipolar Pulse + DC Initiation: Field 4



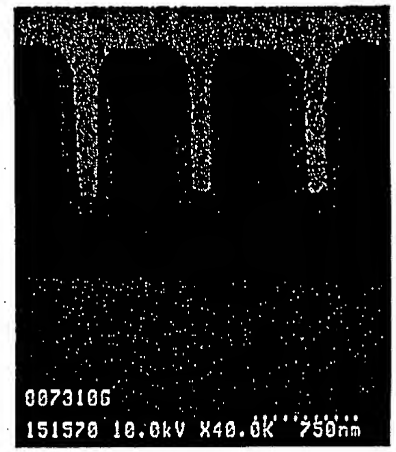
8 sec, 5% 20A



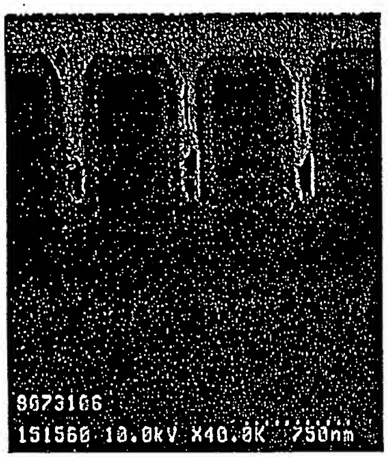
8 sec, 2% 50A



16 sec, 5% 20A



16 sec, 2% 50A

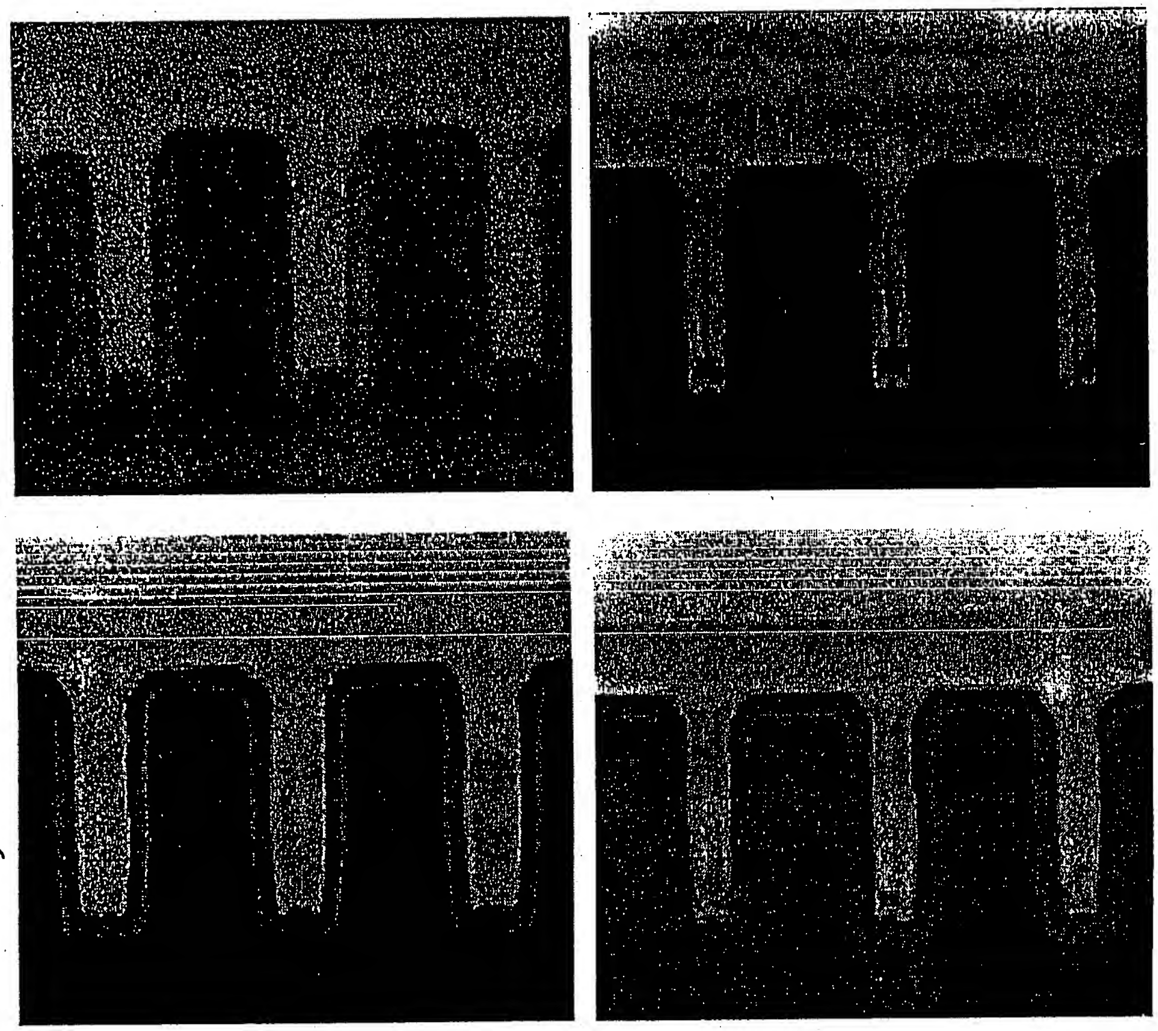


16 sec, 2% 50A
No DC background

-DC background current of 0.5A during initiation
-DC Fill of 7A for 15 seconds

FIG. 44

Initiation + Fill



Rows: 0.5 A, 7.5 sec; 0.5 A, 22.5 sec

Columns: 0.25 µm, 4.8 AR; 0.21 µm, 4.0 AR

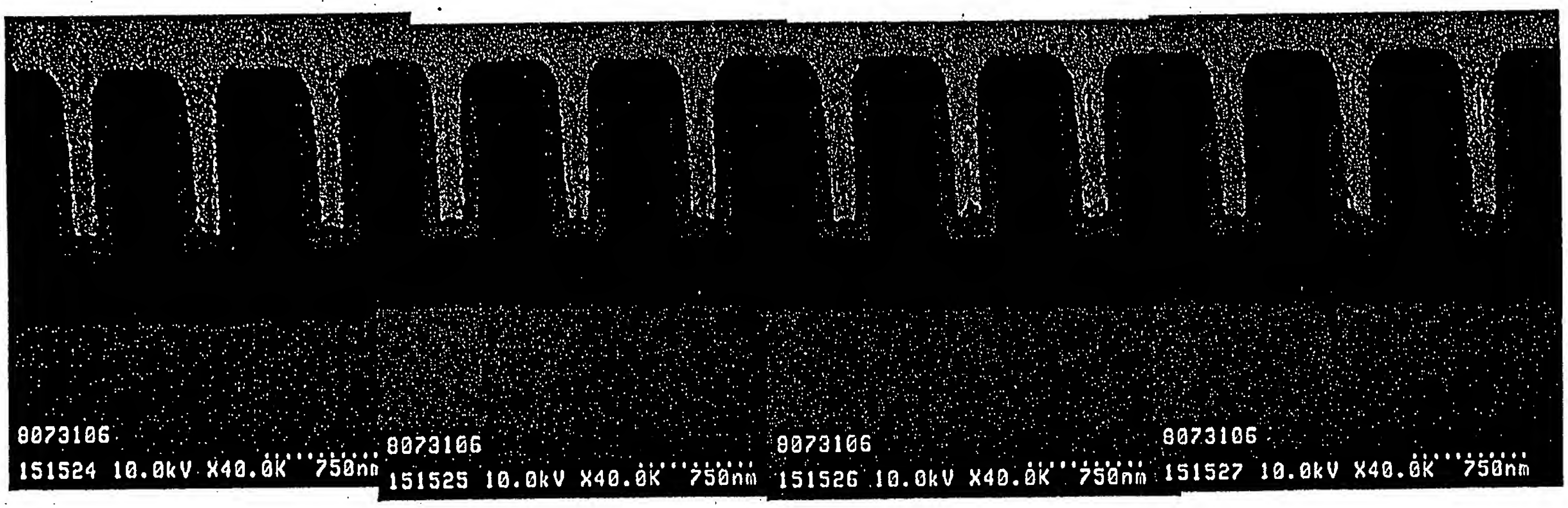
- HCM Cu/Ta
- 1600 Å Cu /250 Å Ta

Conclusion

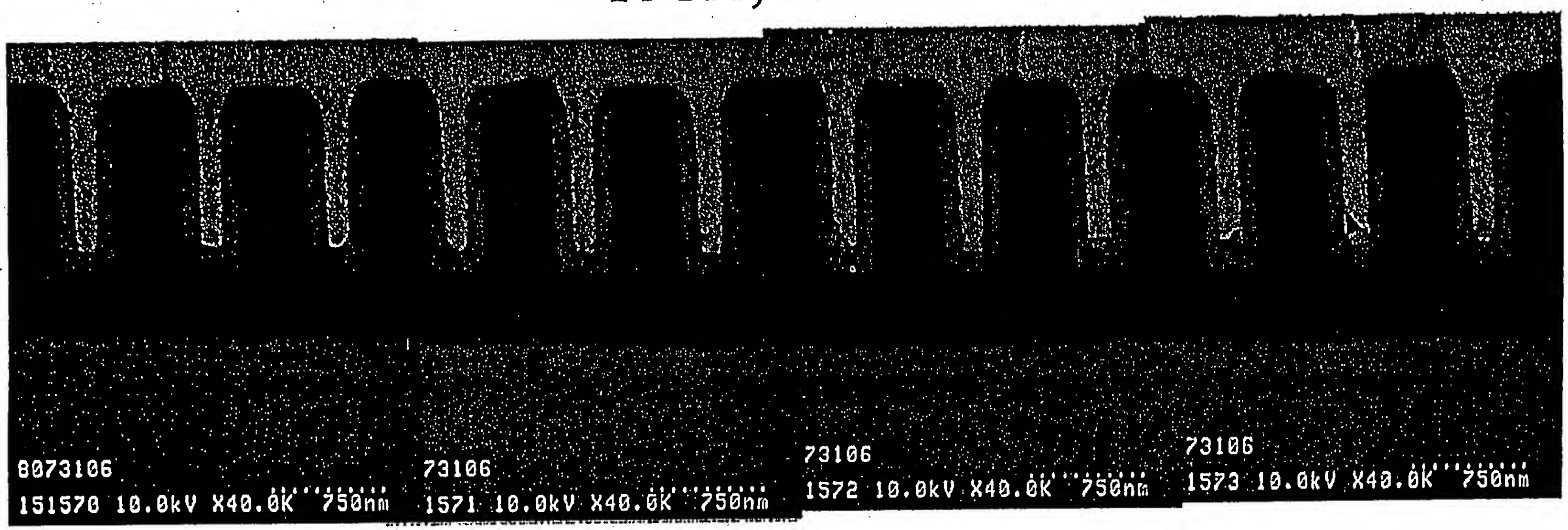
- *Initiation does not build seed at the bottom sidewall*
- *Correlates to final void formation*

FIG. 45

Comparison of 0.5 A Initiation: Unipolar Pulsing Conditions



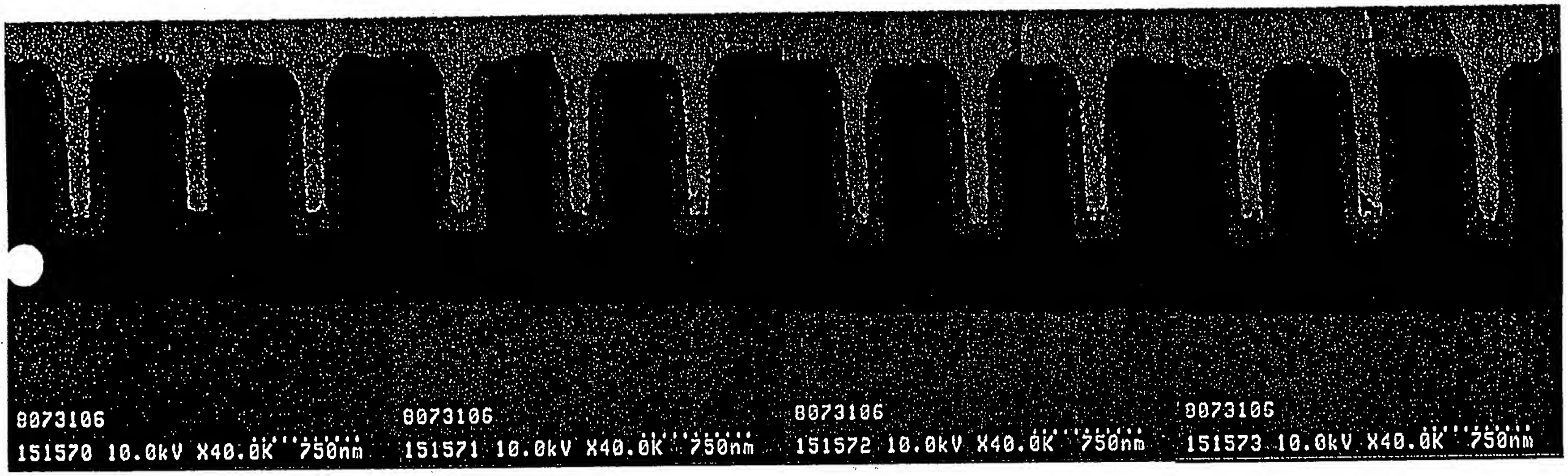
16 sec, 5% 20A



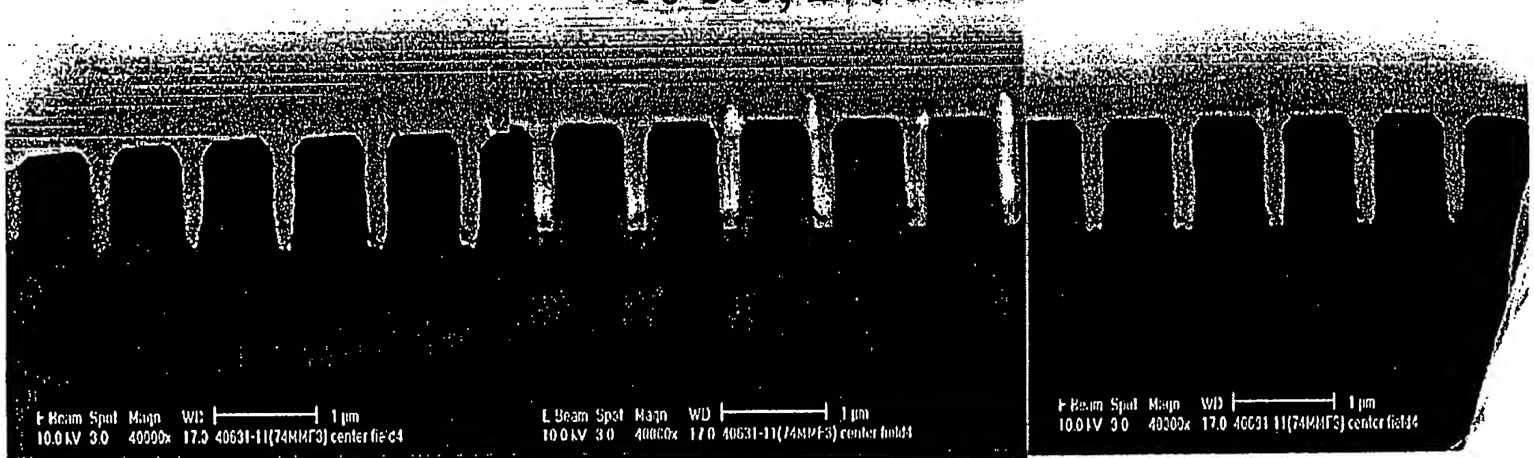
16 sec, 2% 50A

FIG. 46

Comparison of 0.5 A Initiation: With and Without Unipolar Pulsing



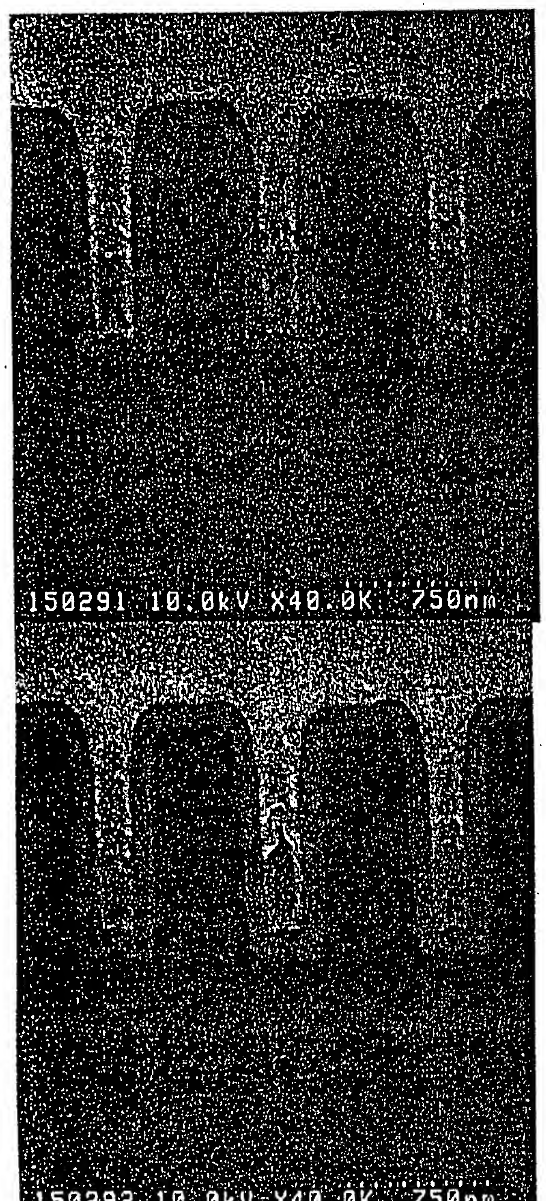
16 sec, 2% 50A



22 sec DC only

FIG. 47

Without Initiation: TI-IMP seed:



- SEMATECH Backfilled via , Field 3 , 0.24 μm x 1.13 μm, AR = 4.7
- Bottom Voids- Yes
- Side wall Voids - No
- Top Void- No
- Center Seam - No
- Film nucleation-poor
- Void % = 90%
- 2 second induction

Barrier/Seed Layer

-TI-IMP
-250Å Ta/1600Å Cu
-Degas Temp. ?
-Sputter etch thickness: ?
-wafer bias: ?

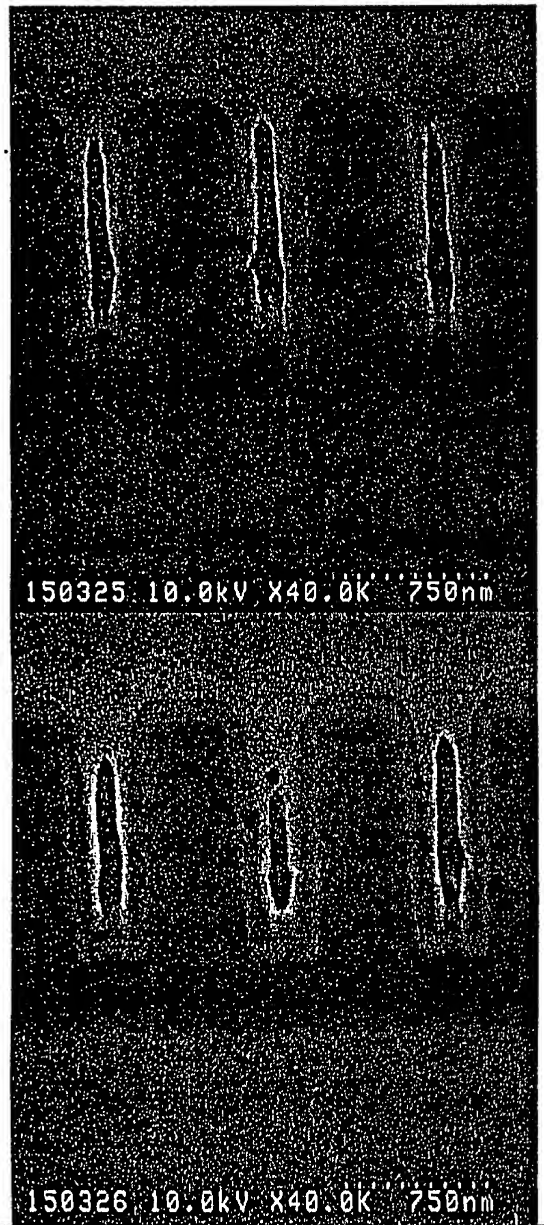
Electroplating

-DC, 7 A
Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

FIG. 48

With Initiation: TI-IMP seed



- SEMATECH Backfilled via , Field 3 , 0.24 µm x 1.13 µm, AR = 4.7
- Bottom Voids- Yes
- Side wall Voids - No
- Top Void- No
- Center Seam - No
- Film nucleation-poor
- Void % = 70%
- 2 second induction

Barrier/Seed Layer

-TI-IMP
-250Å Ta/2200Å Cu
-Degas Temp. ?
-Sputter etch thickness: ?
-wafer bias: ?

Electroplating

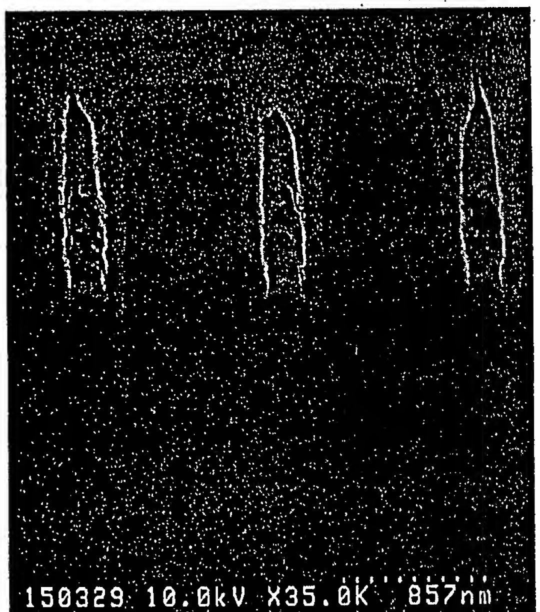
-DC, 1 A, 15 sec then 7 A
Bath Conditions

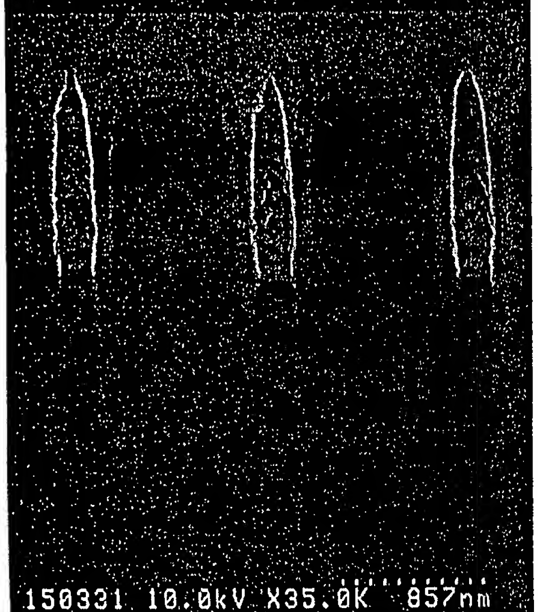
$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

DOSTTT" 5T05T260

FIG. 49

Without Initiation: TI-IMP seed





- SEMATECH Backfilled via , Field 2, 0.29 μm x 1.14 μm, AR = 4.0
- Bottom Voids- Yes
- Side wall Voids - No
- Top Void- No
- Center Seam - No
- Film nucleation-poor
- Void % = 90%
- 2 second induction

Barrier/Seed Layer

-TI-IMP
-250Å Ta/1600Å Cu
-Degas Temp. ?
-Sputter etch thickness: ?
-wafer bias: ?

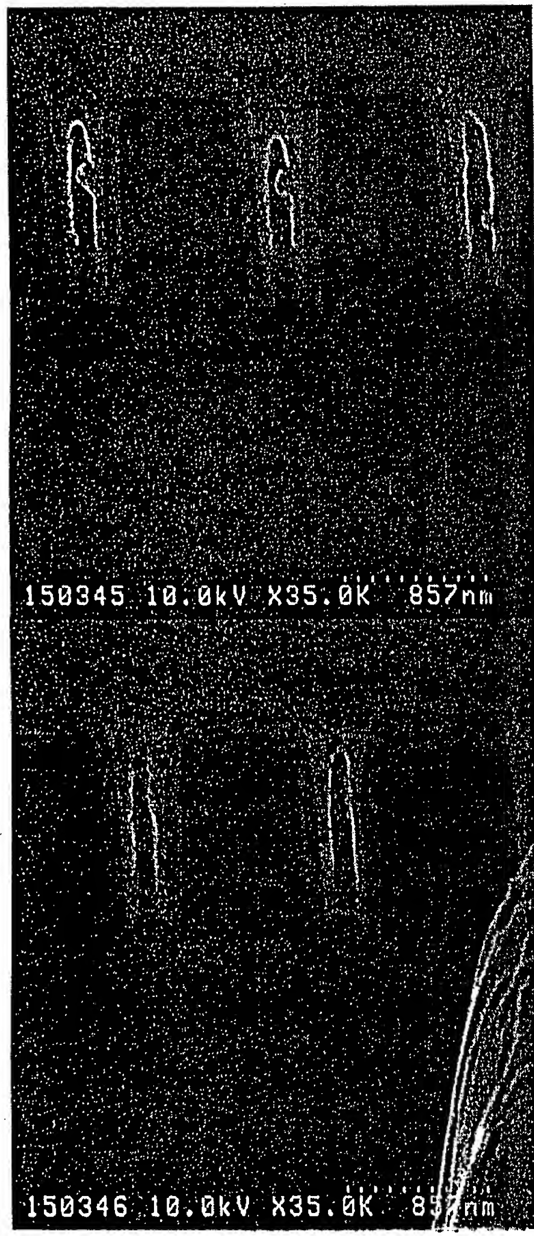
Electroplating

-DC, 7 A
Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^{-}]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

FIG. 50

With Initiation: TI-IMP seed



- SEMATECH Backfilled via , Field 2, 0.29 μm x 1.14 μm, AR = 4.0
- Bottom Voids- Yes
- Side wall Voids - No
- Top Void- No
- Center Seam - No
- Film nucleation-poor
- Void % = 60%
- 2 second induction

Barrier/Seed Layer

-TI-IMP
-250Å Ta/2200Å Cu
-Degas Temp. ?
-Sputter etch thickness: ?
-wafer bias: ?

Electroplating

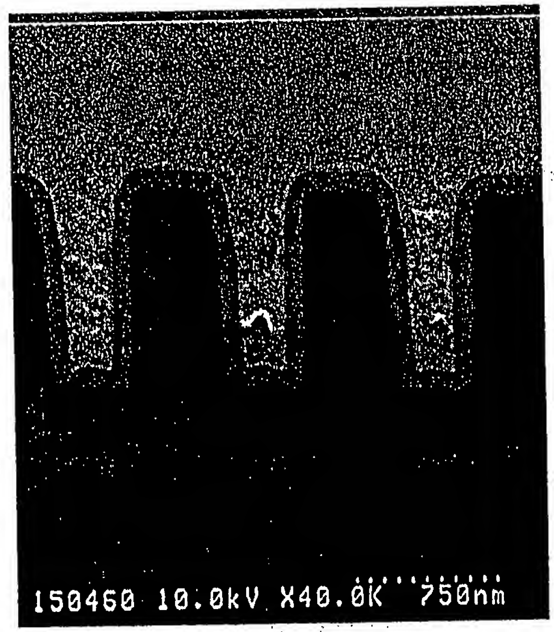
-DC, 1 A, 15 sec then 7 A
Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

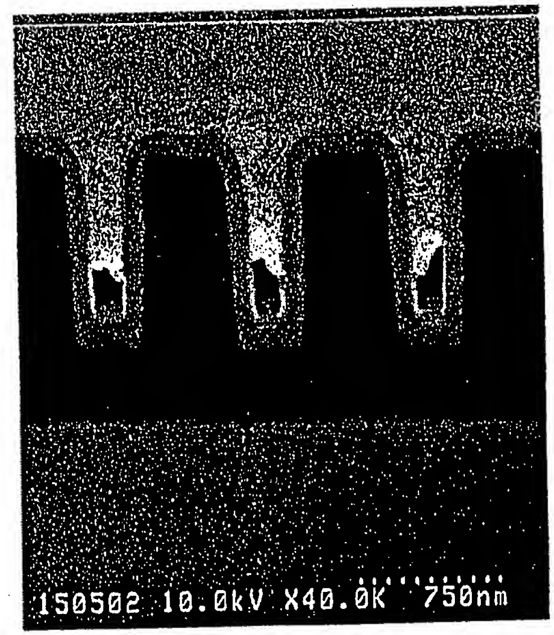
FIG. 51

Initiation: Low current, 2 second induction

Field 2, 0.29 µm x 1.14 µm, AR = 4.0



Field 3, 0.24 µm x 1.13 µm, AR = 4.7
•Void % = 1.3 %



Field 4, 0.2 µm x 1.0 µm, AR = 5.0
•Void % = 15.8 %

- SEMATECH Backfilled via
- TI-IMP Seed
- 250Å Ta/ *1600Å Cu*

Electroplating

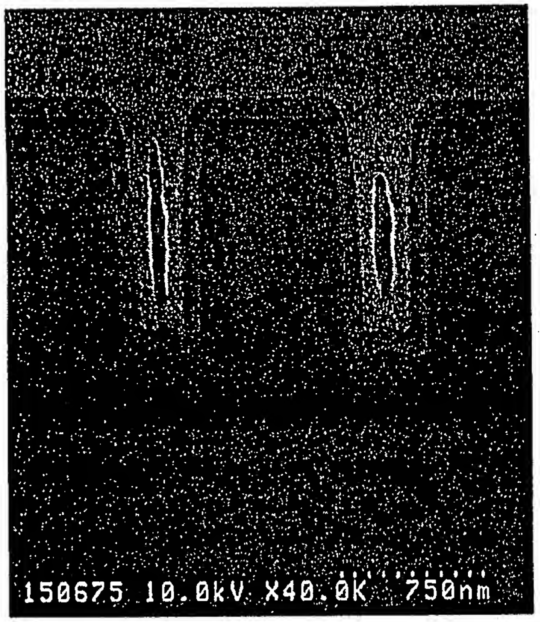
- *Step 1: 1 A for 15 sec*
- *Step 2: DC, 7 A*

Bath Conditions

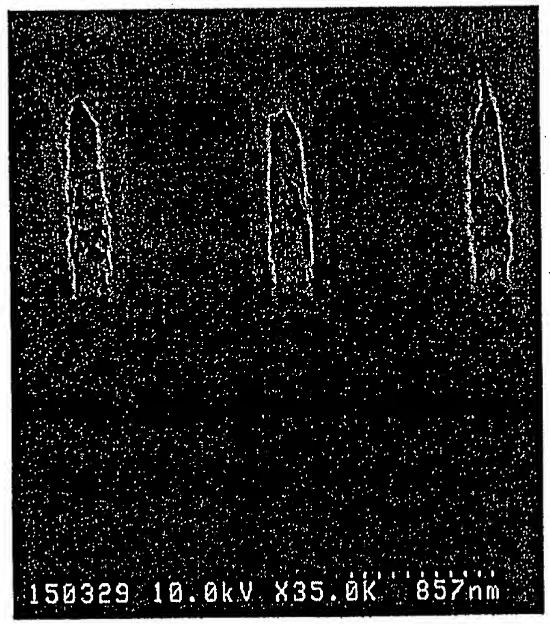
$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125

FIG. 52

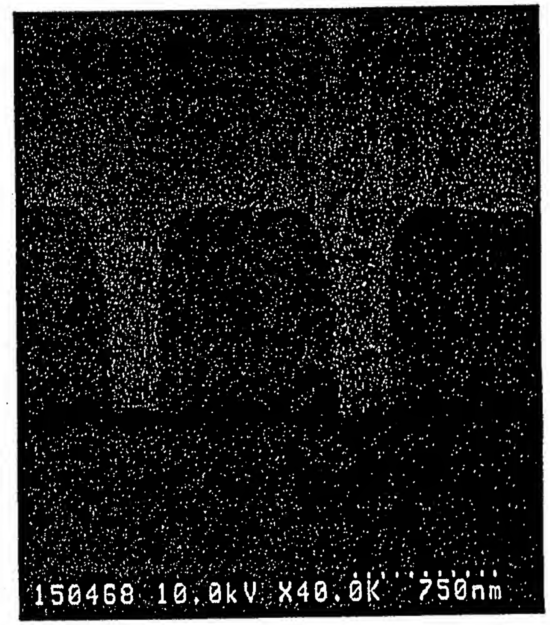
Initiation: Effect of Induction Delay



- *DC, 7 A , 0 sec induction*
- *Void % = 16 %*



- *DC, 7 A , 2 sec induction*
- *Void % = 53 %*



- *Step 1: DC 1 A, 15 sec , 2 sec induction*
- *Step 2: DC, 7 A*
- *Void % = 53 %*

- SEMATECH Backfilled via
- TI-IMP Seed
- 250Å Ta/ *1600Å Cu*

Field 2, 0.29 μm x 1.14 μm, AR = 4.0

Bath Conditions

$[Cu^{+2}]$ = 17.3 g/l	H_2SO_4 = 176 g/l
[MLO] = 3 ml/l	[MD] = 8 ml/l
$[Cl^-]$ = 55 ppm	Temp = 22 °C
Flow = 8 lpm	RPM: 125